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FORT EUSTIS, VIRGINIA

TRECOM TECHNICAL REPORT 63-50

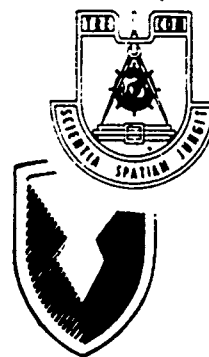
A STUDY OF RAPID SOLIDIFICATION
OF HYDROCARBON FUELS

Task 1D121401A14216
(Formerly Task 9R38-11-009-16)
Contract DA 44-177-TC-819

October 1963

prepared by:

SOUTHWEST RESEARCH INSTITUTE
San Antonio, Texas



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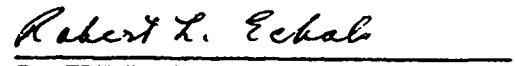
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U S ARMY TRANSPORTATION RESEARCH COMMAND
FORT EUSTIS, VIRGINIA

This research effort was carried out under Contract DA 44-177-TC-819 by the Southwest Research Institute, and was aimed at finding means by which aircraft fuels can be rapidly gelled in an effort to decrease damage and loss of life due to postcrash fires.

The report has been reviewed by the U. S. Army Transportation Research Command and is considered to be technically sound.


The conclusions made by the contractor are considered by this command to be valid.


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A STUDY OF RAPID SOLIDIFICATION OF
HYDROCARBON FUELS

Interim Report

Prepared by

Southwest Research Institute
San Antonio, Texas

for
U. S. ARMY TRANSPORTATION RESEARCH COMMAND
FORT EUSTIS, VIRGINIA

FOREWORD

This program was carried out under Contract DA 44-177-TC-819 covering the period February 15, 1962, to February 14, 1963. Representatives of the U. S. Army Transportation Research Command associated with this program were Lt. Colonel A. M. Steinkrauss, Contracting Officer, and Mr. William J. Nolan, Project Engineer.

The investigation was conducted by Southwest Research Institute, and the program was administrated by the Department of Chemistry and Chemical Engineering under the general direction of Dr. Jan Al, Director. Dr. Jan Al as well as Dr. Leon M. Adams, Manager, Polymers Section, assisted in the technical approach to the problem. The Project Leader was Dr. Eugene C. Martin. Dr. Martin was assisted in the experimental phase of the program by Mr. John D. Millar, Senior Chemist, Mr. John Kaufman, Senior Chemical Engineer, and Messrs. William A. Mallow and Herman W. Schlameus, Associate Chemists.

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SUMMARY

The objective of this research program was to develop methods by which hydrocarbon fuels can be rapidly solidified. The purpose of such an operation would be to solidify fuel in an aircraft fuel tank immediately prior to an impending crash. Frequently, take-off or landing accidents occur in which mechanical damage to the aircraft is not severe, but in which passenger and crew members perish because of the fire which develops very rapidly.

The approach used in this program was to investigate various chemical systems that are capable of forming a gel instantaneously. The most promising approach appeared to be a two-component system. Thus, when a crash appears imminent, a mechanism could be actuated which would inject one of the reactants into the fuel without adversely affecting its burning quality. Should the difficulty be overcome, the plane would continue to fly. However, if the crash was inevitable, a second control could be activated. This would inject the second reactant which would react instantaneously and solidify the fuel.

One system investigated during this program was the reaction of acrylate copolymers with n-tetrabutyl titanate. For example, a copolymer of acrylic acid and 2-ethylhexyl acrylate produced a tough rubber-like gel when reacted with n-tetrabutyl titanate in the presence of JP-4. The reaction as developed to date is too slow; however, by using more reactive organo-metallics, the possibility exists that this system could be utilized in the rapid solidification of fuels.

The most promising fuel solidification system developed during this program involved the reaction of diisocyanates with C₁₂ to C₁₈ fatty amines. Experiments have shown that the type of gel and the speed at which it is obtained can be influenced by the structure of the amine or the diisocyanate. For example, when reacted with lauryl amine in the presence of JP-4, p-phenylene diisocyanate formed a swollen, solid slurry. When reacted with 2,4-tolylene diisocyanate, this same amine formed a product that was soluble in JP-4. However, if the lauryl amine was reacted with a mixture of diisocyanates (65.0 weight percent 2,4-tolylene diisocyanate, 35.0 weight percent 2,6-tolylene diisocyanate), a gel was obtained in concentrations as low as one weight percent. The reaction of pure 2,6-tolylene diisocyanate with lauryl amine was so rapid that good mixing could not be obtained. When the reaction was slowed down by adding n-propyl thiolchloroformate, it appeared that a 2.0 weight percent concentration of additives produced a gel which was estimated

to be as good as was obtained with the mixed isomers at a 4.0 weight percent level.

One of the greatest sources of fire following a plane crash is fuel misting or vaporization. A fuel in this state rapidly reaches explosive concentrations and is readily ignited by a spark. In order to determine how gelling the fuel affects the vapor pressure, gasoline was gelled with 4.0 weight percent additives, and its Reid vapor pressure was compared with that of liquid gasoline. It was found that during the first several hours following gelation, the gelation process significantly decreased the rate of vaporization. Since the gel will not atomize as does liquid fuel and because of the large decrease in the rate of vaporization, the gelation process will practically eliminate the possibility of fire due to fuel misting.

CONCLUSIONS

While the reactions of dibasic acid chlorides with diamines were being investigated, it became apparent that this system should be a good one for fuel solidification since their rates of reaction are extremely rapid. With all of the dibasic acid chlorides tested, only precipitates were obtained. In these tests, commercially available, relatively low-molecular-weight materials were used. Since many of the monomers used produce relatively insoluble polyamide resins of high molecular weight, this precipitation phenomenon could be expected. It is not unrealistic to predict that by the synthesis of specific dibasic acid chlorides and diamines, a system could be developed that will effectively gel fuels, and, since high molecular weight polymers can be obtained by this technique, one would also predict that a strong gel structure could be obtained.

The most promising system developed to date involved the reaction of isocyanates with amines to produce ureas. Numerous experiments were made in which various diisocyanates and amines were reacted in the presence of JP-4. Many of the materials reacted to produce precipitates or soluble products. With respect to the amines as well as to the isocyanates, it was found that a certain type of amine had to be reacted with certain diisocyanates in order to obtain a suitable gel. This is undoubtedly due to the solubility of the resultant urea in the jet fuel. For example, if a particular diisocyanate was reacted with an amine mixture high in unsaturated amines, the resultant urea was soluble; whereas, if the amine mixture was high in saturated amines, a gel was obtained. Experiments have also shown that the quality of a gel can be varied by the choice of isomers of a diisocyanate. For example, if 2,4-tolylene diisocyanate is reacted with lauryl amine in the presence of JP-4, a soluble product is obtained. If a mixture of the 2,4-isomer and the 2,6-isomer is used, the rate of gel formation and the rigidity of the gel increase as the concentration of the 2,6-isomer increases. The pure 2,6-isomer reacts with the amine so fast that good mixing cannot be obtained by pouring the diisocyanate into a rapidly stirred mixture of the amine in JP-4.

The above findings have resulted in systems that will rapidly solidify fuel. A study of the effect of the gel on the vapor pressure of gasoline has shown that during the first several hours, the gel significantly decreases the vapor pressure of the gasoline. This decrease in vapor pressure will undoubtedly decrease the possibility of fires caused by fuel vaporization.

There are some limitations to the systems developed during this program. One important limitation is the temperature. For example, with the amine-diisocyanate system, at temperatures below 0°C there is some difficulty encountered because, at these temperatures, the solubility of the amine in JP-4 is significantly decreased. However, it is felt that with additional effort, an amine or amine mixture could be developed that would greatly extend the temperature limits of this system.

RECOMMENDATIONS

It is proposed that the investigation of the urethanes and ureas as gelling agents for aircraft fuels be continued. To date, several fuel gels have been prepared from urethanes and ureas. It has been shown that the speed at which a gel is obtained can be influenced by the structure of the amine or the diisocyanate. It has also been found that the structure of both the amine and the diisocyanate will, due to solubility effects, influence the properties of the gel.

One system worthy of investigation uses copolymers. For example, acrylic acid was copolymerized with fatty alcohol acrylic esters. These copolymers were solids; however, when dissolved in JP-4 and reacted with n-tetrabutyl titanates, they produced a rubber-like gel. With this system, it would be important to react acrylic acid with other monomers in an effort to obtain low-molecular-weight liquid copolymers. These liquid copolymers could then be reacted with various highly reactive organo-metallics such as the organo-titanate or organo-borates.

Another extremely rapid system is the reaction of dibasic acid chlorides with diamines. The only dibasic acid chlorides tested during this program were those that are commercially available. In the use of these acid chlorides, only precipitates were obtained. This is understandable since these acid chlorides and diamines were developed for the preparation of insoluble polyamides. However, it is felt that a dibasic acid chloride could be synthesized which, when reacted with a specific diamine, would produce a rigid gel.

In systems which produce products which are too insoluble to gel the fuel, solubility may be increased by the introduction of large alkyl groups or halogens. With certain substitutions such as halogen substitution, there is also a possibility of building into the gel a degree of fire retardance.

In an investigation of the afore-mentioned systems, efforts should be directed toward developing a system that will display a satisfactory reaction rate at low (-65°F) as well as at higher temperatures (130°F).

INTRODUCTION

The objective of this research program was to investigate various techniques by which hydrocarbon fuels are rapidly solidified. The purpose of an investigation such as this is to solidify fuel in an aircraft fuel tank immediately prior to an impending crash. Frequently, take-off or landing accidents occur in which mechanical damage to the aircraft is not severe, but in which the passengers and crew members perish because of the fire which develops very rapidly.

The approach used in this program was to investigate various chemical systems that are capable of forming a gel instantaneously. The most promising approach appeared to be a two-component system, in which at least one of the components would not interfere with the combustion properties of the fuel. Thus, when a crash appears imminent, a mechanism could be actuated which would inject one of the reactants into the fuel. Should the difficulty be overcome, the plane would continue to fly, since this material would not affect the burning properties of the fuel. However, if a crash was inevitable, a second control could be activated. This would inject the second reactant which would react instantaneously and solidify the fuel. An accompanying automatic injection system could be installed so that when the tank is ruptured, it would automatically inject both reactants into the tank, thereby gelling the fuel.

DISCUSSION

MALEIC ANHYDRIDE COPOLYMERS

One class of polymers investigated during the course of this program was the copolymers of maleic anhydride. One resin was Gantrez, a copolymer of vinyl methyl ether and maleic anhydride (General Aniline and Film Corp.); the other was SMA resin, which is a copolymer of maleic anhydride and styrene (Texas Butadiene and Chemical Corp.). These resins are insoluble in kerosene; however, by conversion to the half octyl ester, they can be dispersed in the kerosene. The resins are readily converted to the half octyl ester by suspending the resin in octyl alcohol and heating until a clear solution is formed.

A small piece of laboratory equipment was fabricated for the purpose of determining if the products of various reactions would gel JP-4. This equipment consisted of a 6-inch by 3-inch glass pipe which simulated the fuel tank. The base of the tank was equipped with two spray nozzles, each capable of spraying 0.6 gal/hour at 15 psig. Each nozzle was connected to a reservoir which contained one of the reactants. Thus, each of the reactants could be injected into the "fuel tank" and the results observed visually.

The first system investigated was the tetra-isopropyl titanate and the half octyl ester of Gantrez AN119 (maleic anhydride-vinyl methyl ether copolymer). The reactants were charged to the reservoirs, and the system was placed under 12 psig. Only a fraction of the half ester could be pressured into the "fuel tank" before precipitation of the resin plugged the orifice. In an effort to increase the solubility of the resin in the JP-4, the Gantrez resin was converted to the half stearyl ester. This resin could be readily injected into the fuel. Due to its increased solubility, the reaction product of the half stearyl ester and n-tetrabutyl titanate failed to gel the fuel.

Since the stearyl ester failed to form a gel due to the high solubility and since the octyl ester failed because of insolubility in the JP-4, the Gantrez resin was reacted with an 80/20 mixture of lauryl alcohol-myristyl alcohol to yield the corresponding mixed half ester. However, this also failed to gel when injected into the fuel with the tetraisopropyl titanate.

The previous experiments have shown that the half octyl ester of Gantrez is too insoluble in the fuel to be suitable, whereas the half stearyl ester is too soluble. Intermediate esters likewise failed to yield a satisfactory gel when reacted with tetraisopropyl titanate. As a result, the Gantrez resin was abandoned, and attention was turned toward the SMA resin (styrene-maleic anhydride copolymer). Using the dodecyl half ester and tetraisobutyl titanate failed to yield a desirable gel. Since the half ester of the maleic anhydride portion of the polymer chain contains a free carboxyl group, various attempts were made to inject the half ester into the fuel and to try to gel it by adding an amine which would convert it to the amine salt. The failure to obtain a suitable gel was probably due to the high solubility of the product in the JP-4 fuel.

It is known that a mixture of a high-molecular-weight acid and a fatty amine will form a salt, although the rate of salt formation is relatively slow as compared to that of lower-molecular-weight compounds. Previous experiments have also shown that the fatty amine salt of the dodecyl and stearyl half ester of SMA (styrene-maleic anhydride copolymer) are soluble in the jet fuel. Therefore, if a fast-reacting, crosslinking agent is reacted with a soluble salt, a gel should be obtained. Tolylene diisocyanate was chosen as the crosslinking agent since it rapidly reacts with an amine as well as with a free carboxyl group. Table 1 lists some typical experiments made with various amine salts of the SMA resin and tolylene diisocyanate. The tolylene diisocyanate used in these experiments was Hylene TM-65 (product of Du Pont) and consists of mixed isomers. In run I-18A, the octyl half ester of SMA-2000 was converted to the amine salt by reaction with diethylene triamine. This salt was then injected into the fuel. Sufficient tolylene diisocyanate was then injected to give a total of 17.65 weight percent additives and 82.35 weight percent fuel. This system produced a firm, dry gel very rapidly. Since the total weight of additives was entirely too high, efforts were made to decrease this weight. However, as shown in run I-19A, when the total weight of additives was decreased to 11.3 weight percent, only a thick slurry was rapidly obtained, and additional tolylene diisocyanate had to be added to obtain gelation. The use of the half dodecyl ester of SMA-2000 with ethylene diamine and tolylene diisocyanate yielded only a thick slurry and required periods of up to 30 minutes before a firm gel was obtained.

POLYAMIDES AS POTENTIAL GELLING AGENTS

One of the more promising approaches undertaken during the course of this program was the investigation of various polyamides. The reaction of a dibasic acid chloride and a diamine is an extremely rapid one, thus making it a potential gelling system for jet fuels.

It is recognized that in order to avoid precipitation of the polyamide in the fuel, either the diamine or the dibasic acid chloride should contain a long alkyl or other groups in order to add fuel solubility to the resultant polymer. The technique initially employed was to inject the dibasic acid chloride into the JP-4. A mixture of the diamine, caustic (required to neutralize the hydrochloric acid liberated), water, and surfactant was then injected into the fuel. The idea was to form an oil-in-water emulsion. The diamine and dibasic acid chloride react at the oil/water interface and form a polyamide film which in essence encapsulates the fuel. Repeated experiments revealed that the quantity of water and surfactant needed to form an acceptable emulsion was entirely too high. As a result, attempts were made to gel fuels by producing a polyamide that would be highly swollen in the fuel, thus producing a gel.

In order to evaluate various polyamides, a series of polymerizations were made in JP-4. Typical experiments are listed in Table 2. The various amines tested are commercially available fatty amines as obtained from Armour Chemical Company and General Mills. In run number 3-1-1, Diam-21 (N-Coco-1, 3-propylene diamine) when reacted with sebacoyl chloride in the presence of JP-4 produced a flocculent suspension, whereas this same amine when reacted with phthaloyl chloride formed a soluble product which thickened the fuel.

After various diamines were tested, it was decided to determine what effect the product of a monoamine and a dibasic acid chloride would have on JP-4. In run number 3-1-5 as listed in Table 2, Alamine 21D (Coco amine) was reacted with sebacoyl chloride in JP-4. The product gelled the fuel, although the gel was very weak. This same amine when reacted with phthaloyl chloride thickened the fuel, but it did not form a gel. These results indicate that by synthesizing the proper diamine and/or dibasic acid chloride, a system could be developed that would effectively gel fuels.

Since previous experiments indicated that some degree of solubility had to be built into the polyamide, several diamines containing long alkyl groups were prepared. These diamines were prepared by reacting Empol 1014, a dimer acid (manufactured by Emery

Industries), or dodecenyl succinic anhydride with various amines to produce the corresponding amides containing amine groups. The syntheses of these amines are listed in the experimentation section. The modified amines were reacted with sebacoyl chloride in the presence of JP-4. The results of these tests are listed in Table 3. The reaction was an extremely rapid one, but in no instance was a gel formed.

ATTEMPTED FUEL SOLIDIFICATION BY USING VARIOUS EPOXIDES

Another class of compounds investigated during the course of this program was the epoxides. These compounds are known to react with various compounds to yield polymeric materials. Numerous catalysts or curing agents were investigated in order to find one that would react rapidly with epoxides. Two of these were tri-m, p-cresyl borate and EM550, an epoxy catalyst manufactured by Thiokol. The latter, however, was insoluble in JP-4, a factor which eliminated it as a catalyst. In run number 3-3-1, as listed in Table 4, Oxiron-2001, an epoxy polymer manufactured by FMC Corporation, was reacted with tri-m, p-cresyl borate to produce rapidly a heavy precipitate in JP-4. Araldite-506 (manufactured by Ciba), another epoxy polymer, likewise produced a precipitate when reacted with tri-m, p-cresyl borate in JP-4. Since the reacted epoxides were insoluble in JP-4, several attempts were made to utilize epoxy monomers as one of the reactants. The results of these experiments are listed in Table 5. In run number 3-8-1, vinylcyclohexene diepoxide was reacted with tri-m, p-cresyl borate in the presence of JP-4 to form a gummy precipitate which rapidly agglomerated and settled to the bottom of the container. In run number 3-8-5, the same diepoxide was reacted with a mixture of tri-m, p-cresyl borate and Niox 1025 [a poly (propylene glycol) having an average molecular weight of approximately 1000] to produce a voluminous precipitate in the presence of JP-4. The precipitate slowly agglomerated and formed a gummy precipitate on the bottom of the container. The remainder of the materials tested did not show any promise, in that the products were either soluble in the fuel or produced a slight precipitate.

FUEL GELATION BY USING POLYUREAS

One of the more important requirements in developing a fuel gelation system is that the reaction must be very fast, since time is of the utmost importance immediately prior to an impending crash. These requirements are met by the amine-diisocyanate reaction which forms polyureas.

It was previously stated in the section on maleic anhydride copolymers that the amine salts of the half esters of styrene-maleic anhydride resins are soluble in JP-4. When these materials were reacted with tolylene diisocyanate, only slurries were obtained even at high concentrations. In addition, a relatively long reaction time was required to obtain a gel. It is known that amines react quite rapidly with diisocyanates; therefore, the presence of the styrene-maleic anhydride as the amine salt has significantly altered the rate of reaction. As a result of these findings, a series of experiments were initiated in an effort to gel the fuel by using substituted polyureas. Typical examples are listed in Table 6.

In run number 1-30-1, Armeen 12, a mixture of primary fatty amines which is primarily dodecyl amine (Armour Chemical Company) was injected into the fuel and followed by Hylene TM-65 (65 weight percent 2,4-tolyene diisocyanate, 35 weight percent 2,6-tolyene diisocyanate). A total of 5.5 weight percent additives produced a firm, dry gel in a few seconds. In the succeeding experiments, the amount of total additives was decreased in an effort to determine the minimum quantity required to produce a firm, dry gel. At a concentration as low as 1.0 weight percent, a firm gel was obtained; however, the gel was broken into a thick slurry with stirring. It is realized that in actual application, the solidified fuel will not be stirred; however, on impact, the fuel tank might be ruptured; the momentum would then force the gelled fuel through the hole in the tank and subject the gel to shear. It should be pointed out that even though the gel is broken and will probably be forced through the hole in the ruptured tank, the nature of the gel is such that it will practically eliminate the problem of fuel misting, which is an important factor in the initiation of fires following a plane crash. Also, the gel will prevent fuel from flowing under the fuselage.

Efforts were then directed toward the use of polyfunctional amines with the Armeen 12. The reason for this is that the polymeric chain can be increased by using a small amount of polyfunctional amines. With a higher molecular weight, a firmer gel should be obtained. The first approach toward obtaining the higher molecular weight was to react mixtures of the Armeen 12 and various polyamines with the tolylene diisocyanate (Hylene TM-65). Typical experiments are listed in Table 6. In run number 1-31-9, Duomeen S, which is primarily N-stearyl-1,3-propylene diamine (Armour Chemical Company), was blended with the Armeen 12 and reacted with Hylene TM-65. The resultant gel was approximately the same as that obtained when only Armeen 12 was used. Since there was no improvement in the rigidity of the gel when fatty diamines were used, run number 1-34-4 was made,

using ethylene diamine. In this experiment, only a precipitate was obtained. This was probably because the diisocyanate will react selectively with the ethylene diamine because of its greater reactivity. Examination of the results listed in Table 6 shows that the other amines which were blended with Armeen 12 yielded either inferior gels or precipitates.

Since a relatively low-molecular-weight material is obtained when a primary amine is reacted with a diisocyanate, a series of N-substituted propylene diamines (manufactured by General Mills) were reacted with Hylene TM-65 in the presence of JP-4. In addition, several primary amines manufactured by General Mills were investigated at the same time. The results of these tests are listed in Table 7. It may be observed that the substituted 1,3-propylene diamines when reacted with the diisocyanate gave soluble products. The one exception to this was the N-Coco-1,3-propylene diamine, which gave a swollen precipitate in JP-4. It may be noted in Table 7 that the primary fatty amines gave a weak to firm gel when reacted with Hylene TM-65 in JP-4. The Alamine 4D is essentially the same as Armeen 12, which is manufactured by Armour Chemical Company. It was also expected that the Coco amine would give a gel, since its main constituent is lauryl amine.

It was previously stated that the adduct formed by the reaction of Armeen 12 and Hylene TM-65 (tolylene diisocyanate) would gel JP-4 in concentrations of 1 weight percent. The gel remained rigid; however, it could be broken by stirring. After the gel was broken, the pieces remained rigid and there was no tendency to flow. However, when a small piece of the gel was placed on aluminum and ignited, the gel melted with some degree of flowing. It was found that increasing the additives to 2 weight percent significantly decreased the flow after ignition. When burning 50 gms of the gel on a piece of aluminum, there was little or no flowing until approximately half had burned. As a result, an effort was made to obtain an improved gel by blending various compounds with the Armeen 12 prior to reacting it with the TM-65. Several of these tests are listed in Table 8. It may be noted that the addition of butyl rubber or polyisobutylene gave inferior gels. In run number I-42-2 an effort was made to combine chemically the additive to the Armeen 12-TM-65 adduct. This was accomplished by reacting triethylene tetramine with polybutadiene/acrylic acid copolymer to yield the corresponding amide. The procedure for this synthesis is listed in the experimentation section. A mixture of the amide and Armeen 12 was dissolved in JP-4 and then reacted with tolylene diisocyanate. The resulting polymer did not form a gel but produced a thick slurry.

While the Armeen 12-tolylene diisocyanate adduct was being considered, several tests were made to determine the optimum weight ratio of tolylene diisocyanate to Armeen 12. Two of these runs are listed as I-34-1 and I-40-1 in Table 8. It may be observed that a better gel was obtained with a tolylene diisocyanate to Armeen 12 ratio of 0.4/1 than with a 0.8/1 ratio. Furthermore, the better gel was obtained by using a smaller quantity of additives.

In run number I-34-1 as listed in Table 6, it was reported that a precipitate was obtained when Hylene TM-65 was reacted with diethylene triamine. Therefore, several experiments were made in which the diethylene triamine was modified prior to reaction with the diisocyanate. The purpose of the modification was to attempt to increase the solubility of the product in JP-4. The diethylene triamine was modified by reaction with various acid chlorides or alkyl halides. The compounds synthesized are listed as modified diethylene triamines in Table 9. In runs numbered 2-35-1 and 2-35-3, the product obtained by reacting the modified diethylene triamine with Hylene TM-65 in JP-4 was swollen by the fuel, whereas unmodified diethylene triamine reacted with the diisocyanate in JP-4 gave a fine precipitate. In runs numbered 2-35-4 and 2-35-5, the modifying group was such that the resulting polymer was soluble in JP-4.

During the investigation of various polyurea systems, it was noted that the best gels were obtained by reacting Hylene TM-65 with Alamine 4D (primarily lauryl amine) or Alamine 21D (Coco amine). If one considers the possible structures of the resultant products, it is apparent that no high molecular weight product is formed. The highest molecular weight combination that can exist is the reaction product of two moles of the amine with one mole of the diisocyanate. The possibility exists that some of the diisocyanate can react with the urea linkage in the afore-mentioned adduct. The residual isocyanate groups can then react with other urea linkages to double the molecular weight approximately. However, it is felt that this reaction is secondary, since the rate of reaction between a primary amine and an isocyanate group is much faster than the reaction rate of an urea linkage and an isocyanate group. As a result, a series of tests were made in order to determine if jet fuel could be gelled by using mono-isocyanates and various amines as the gelling agents. The first of the mono-isocyanates investigated was phenyl isocyanate. The results of these tests are listed in Table 10. It may be observed that the product obtained by reacting phenyl isocyanate with the substituted propylene diamines either formed precipitates or were soluble in JP-4. Increasing the equivalent ratio of isocyanate to amine

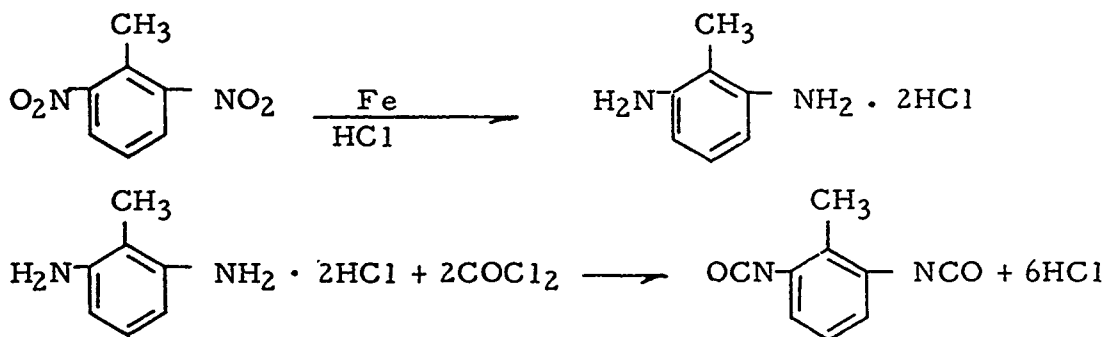
(to assure reaction of the isocyanate with the urea linkage) failed to change the solubility properties of the products in JP-4 significantly. It may be noted that the product obtained by reacting phenyl isocyanate with Alamine 4D approached a gel in that it formed a highly swollen suspension. Attempts were made to gel fuel by mixing a small amount of tolylene diisocyanate with the phenyl isocyanate prior to reacting it with the Alamine 4D. This likewise failed to produce a satisfactory gel.

The second mono-isocyanate investigated during the course of this program was m-tolyl isocyanate. The results of these tests are listed in Table 11. If one compares the results obtained when m-tolyl isocyanate or phenyl isocyanate was reacted with Diam 11 (N-oleyl-1, 3-propylene diamine), he will find that the m-tolyl adduct was soluble in JP-4, where as the phenyl adduct formed a precipitate. It may also be noted that when Alamine 4D (lauryl amine) was reacted with m-tolyl isocyanate, the product formed a slight precipitate in JP-4. When reacted with phenyl isocyanate, the same amine also produced a precipitate, but it was highly swollen and formed a thick slurry in JP-4.

During the investigation of various polyurea systems using various amines and diisocyanates, it was observed that the structure of both the diisocyanate and the amine influences the properties of the gel as well as the rate of gel formation. As a result of these findings, a series of experiments was initiated in which various diisocyanates were synthesized and evaluated. The preparation of the various diisocyanates are listed in the experimentation section. The first of the diisocyanates to be synthesized was p-phenylene diisocyanate. The evaluation of p-phenylene diisocyanate and various amines as potential gelling agents is listed in Table 12. It may be observed that the various diamines formed precipitates or formed a very weak gel with this diisocyanate in the presence of JP-4. It may also be observed that when Alamine 4D and Alamine 21D were reacted with p-phenylene diisocyanate, the resultant products formed a swollen, solid slurry in the fuel but did not produce a gel. These same amines, when reacted with tolylene diisocyanate (65 weight percent 2, 4-isomer and 35 weight percent 2, 6-isomer) form a firm gel.

With respect to the commercial availability of the tolylene diisocyanates, one can readily obtain pure 2, 4-tolylene diisocyanate, a mixture consisting of 65 weight percent 2, 4-tolylene diisocyanate and 35 weight percent of the 2, 6-isomer and a second mixture consisting of 80 weight percent 2, 4-tolylene diisocyanate and 20 weight percent of the 2, 6-isomer. Previous experiments utilizing the various tolylene diisocyanates seemed to indicate that 2, 6-tolylene diisocyanate was the isomer in the diisocyanate mixture that produced the gel in JP-4.

As a result, the 2,6-isomer was synthesized. Because of the lack of availability of 2,6-diaminotoluene, it was necessary to start with 2,6-dinitrotoluene and reduce it to the diamine by using iron and hydrochloric acid. The diamine dihydrochloride was then reacted with phosgene to produce the diisocyanate. The general reactions are illustrated as follows:



The 2,6-tolylene diisocyanate was then reacted with various amines in the presence of JP-4. The results of these tests are listed in Table 13. With all of the amines tested, the rate of reaction was so fast that it was impossible to obtain good mixing in the laboratory. The technique used to mix the two reactants was to add the amine to the fuel and then while rapidly stirring the fuel to add the diisocyanate. In run number 5-24-3, the rate of reaction was retarded by mixing n-propylthiolchloroformate with the diisocyanate and adding this mixture to the fuel containing the amine. In this experiment a good gel was obtained by using only 2 weight percent additive, based on the weight of the fuel.

In run number 5-24-4, oleyl amine was reacted with 2,6-tolylene diisocyanate to produce a clear, weak gel. The gel was much different from those obtained with other amines in that it displayed some elastic properties. This gel elasticity has not been observed with other fuel gels prepared from the amine-diisocyanate system. With the commercially available diisocyanate mixtures, oleyl amine does not form a gel.

While gels using 2,6-tolylene diisocyanate as one of the reactants were being made, it became apparent that in the tolylene diisocyanate-amine system, it is the 2,6-isomer that produces the fuel gel and not the 2,4-isomer. As previously reported, the tolylene diisocyanates commercially available are (1) 2,4-tolylene diisocyanate, (2) a mixture of 80 weight percent 2,4-tolylene diisocyanate and 20 weight percent 2,6-tolylene diisocyanate, and (3) a mixture of 65 weight percent of the 2,4-isomer and 35 weight percent of the 2,6-isomer. A comparison was made of the results obtained by reacting the various tolylene diisocyanate mixtures with lauryl amine (Alamine

4D). The results of this comparison are listed in Table 14. It may be observed that when pure 2,4-tolylene diisocyanate is reacted with lauryl amine in JP-4, a soluble product is obtained. As the concentration of the 2,6-isomer increases, the rate of gel formation and the rigidity of the gel increase. The pure 2,6-isomer reacts with the amine so fast that good mixing cannot be obtained by pouring the diisocyanate into a rapidly-stirred mixture of the amine in JP-4.

In summarizing the results obtained with aromatic isocyanates and diisocyanates, reference is made to Table 12, where p-phenylene diisocyanate was reacted with lauryl amine. The reaction product formed a thick slurry in JP-4 instead of a gel. As stated earlier in this report, 2,4-tolylene diisocyanate with lauryl amine yielded a soluble product in JP-4. When mixtures of 2,6-tolylene diisocyanate and 2,4-tolylene diisocyanate were reacted with lauryl amine, the rigidity of the gel increased with the concentration of the 2,6-isomer in the mixture. Moreover, the pure 2,6-tolylene diisocyanate reacted so fast that proper mixing could not be obtained in the laboratory. When this reaction was slowed down by adding 10 weight percent (based on the diisocyanate) n-propyl thiolchloroformate, it appeared that a 2 weight percent concentration of additives produced a gel which was estimated to be as good as that obtained with the mixed isomers at a 4 weight percent level.

It was previously stated that the structure of the amine significantly influences the properties of the gel. It is also realized that if a diamine is used in place of a monoamine, a much higher molecular weight can be obtained. In an effort to increase the rigidity of the gel, several commercially available diamines were evaluated with various isocyanates and diisocyanates.

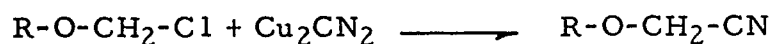
One of the diamines evaluated was dimer diamine. This material is the diamine of dimer acid, as produced by Emery Industries. The results of the evaluation of this diamine in the presence of jet fuel are listed in Table 15. On examination of the results, one may observe that the products range from an immiscible oil to a highly swollen precipitate but that none of the systems tested would gel JP-4.

m-Xylene diamine was also evaluated in an effort to determine if it would solidify jet fuel when reacted with various diisocyanates. The results of these tests are listed in Table 16. It may be observed that, with all of the diisocyanates tested, the m-xylene diamine-diisocyanate adduct produced a precipitate in the presence of jet fuel.

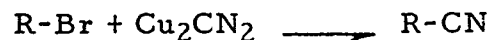
Since the commercially available diamines failed to gel jet fuel when reacted with various diisocyanates, a program was initiated to synthesize various diamines and triamines. The starting materials for the syntheses of the afore-mentioned diamines were the Ethomeens (ethylene oxide adducts of fatty amines as manufactured by Armour Chemical Company) and the Propomeens (propylene oxide adducts of fatty amines) as well as poly(ethylene glycols) and poly(propylene glycols) having various molecular weights. The starting materials for preparing the triamines were various triols such as the polyoxypropylene derivatives of trimethylolpropane.

Various approaches were attempted in synthesizing the amines from the corresponding alcohols. For the purpose of simplicity, the general reactions are listed below, using mono-alcohols in place of the respective diols and triols.

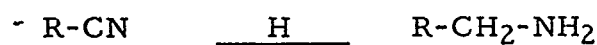
1. Chloromethylation



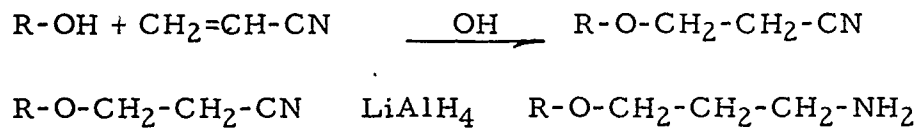
2. Halogenation, using anhydrous Hydrogen Bromide



3. Halogenation, using Thionyl Chloride



4. Cyanoethylation



With respect to the chloromethylation reaction, several derivatives were prepared by using various Pluracols as the starting diols. The Pluracol diols are polyoxypropylene adducts of propylene glycol. The technique consisted of mixing trioxane with the diol and bubbling in anhydrous hydrogen chloride. After the reaction was complete, the excess hydrogen chloride was removed by bubbling dry nitrogen through the α -chloromethyl ether since the α -chloromethyl ether is moisture sensitive. This proved to be a time-consuming process and did not appear to be a satisfactory procedure for preparing various amines for screening purposes.

After the dissolved HCl was removed, the α -chloromethyl ether was reacted with cuprous cyanide in order to obtain the corresponding nitrile. This consisted of suspending the cuprous cyanide in benzene, heating to 40°C, and adding the α -chloromethyl ether by drops over a two hour period. On completion of the reaction, the remaining cuprous cyanide and cuprous chloride were removed by filtration. To avoid the handling of a voluminous precipitate as is obtained when LiAlH₄ is used as a reducing agent, the dinitriles were reduced with sodium and butanol. During the reduction reaction, considerable quantities of ammonia were liberated, indicating that cleavage was occurring. As a result, this approach was abandoned.

The second approach considered was the halogenation of the alcohol by using anhydrous hydrogen bromide. One experiment was made in which PPG-1025 poly(propylene glycol) (average molecular weight of 1000) was used as the starting material. While bubbling in the anhydrous hydrogen bromide, the diol adsorbed an excessive amount of the gas. An attempt to isolate the product by vacuum distillation clearly indicated that the hydrogen bromide had cleaved the ether linkages of the poly(propylene glycol).

Various attempts were made to prepare the chlorine derivatives of the Ethomeens (ethylene oxide adducts of fatty amines) by reaction with thionyl chloride. The results indicated that the thionyl chloride degraded the Ethomeens in that a water-soluble, black, wax-like solid was obtained.

Attention was then directed toward the cyanoethylation reaction. This reaction had an advantage in that only two steps are required in converting the alcohol to the corresponding amine. An additional advantage is that the presence of ether linkages and tertiary amine groups as are present in the Ethomeens and Propomeens are not affected by the cyanoethylation reaction. Several diols and triols were cyanoethylated by using sodium methoxide or potassium hydroxide as the catalyst. Since the cyanoethylated products were high boiling, viscous materials, the products were reduced by using sodium and butanol without purification. In the reduction step, it was noted that not all of the sodium had reacted. On further investigation, it was found that some difficulty was encountered in the cyanoethylation reaction. The condensation of the acrylonitrile with the alcohol is base-catalyzed. Since the polymerization of acrylonitrile is also base-catalyzed, the two reactions are competing with one another. It was found that by using either sodium methoxide or potassium hydroxide as the catalyst, the rate of reaction for the polymerization of acrylonitrile was greater than the rate of reaction for the condensation of the high-molecular-weight diol or triol with acrylonitrile. This resulted in a low yield of the cyanoethylated product.

In view of the difficulties encountered with the sodium methoxide and potassium hydroxide catalysts, attention was directed toward the use of Triton B (tetramethylammonium hydroxide) as the catalyst. One experiment was made in which poly(propylene glycol) (molecular weight of 150) was condensed with acrylonitrile by using Triton B as the catalyst. By the use of this catalyst, a high yield of the corresponding dinitrile was obtained. Reduction of the dinitrile to the corresponding diamine was accomplished by using lithium aluminum hydride as the reducing agent. The diaminoethyl adduct of poly(propylene glycol) (molecular weight 150) was evaluated with several aromatic diisocyanates in the presence of JP-4. Only precipitates were obtained; this indicated that a more hydrophobic group is needed. This might be accomplished by using the Ethomeens or Propomeens as the starting diol in the synthesis of the diamine.

FUEL GELATION BY USING POLYURETHANES

During the investigation of the polyurea systems, it was realized that the structure of both the amine and the diisocyanate significantly influences the properties of the resultant fuel gel. It is known that the reaction of a diol and a diisocyanate is very rapid, especially if suitable catalysts are employed. Therefore, it became appropriate to consider the diol-diisocyanate system as well as prepolymers prepared by reacting diols with an excess of diisocyanate. The isocyanate terminated prepolymer can then be reacted with diamines in the presence of jet fuel.

Of the various commercially available urethane polymers investigated, only a few were soluble in JP-4. One of these was Adiprene L-100, a urethane elastomer manufactured by Du Pont. This polymer was reacted with various amines and polyamines. Typical experiments are listed in Table 17. Using Armeen 12 as the co-reactant, it failed to form a gel. Other amines tested were Araldite DP-125 (Ciba) and Genamid 250 (General Mills). These compounds produced a gummy precipitate which separated from the fuel.

A program was then initiated to prepare urethane prepolymers that are soluble in jet fuel. The first prepolymer investigated was the one obtained by reacting 0.5 mole of Niax PPG-1025 poly(propylene glycol) (manufactured by Union Carbide Chemicals Company) with 1.06 moles of Hylene TM-65 (mixed isomers of tolylene diisocyanate manufactured by Du Pont). This prepolymer was then reacted with various amines. A series of these tests are listed in Table 18. In run number 2-38-1, the prepolymer was reacted with lauryl amine. The resultant product gave a weak gel. In an effort to increase the firmness of the gel, several substituted 1,3-propylene diamines were used. As shown in Table 18, the products formed only flocculent precipitates in JP-4.

It may be observed from Table 18 that only the primary fatty amines gave gels when reacted with the Niax PPG-1025-Hylene TM-65 prepolymer. Other prepolymers were prepared by reacting various poly(propylene glycols) such as Niax PPG-2025 with Hylene TM-65; however, these prepolymers were only slightly soluble in JP-4. Table 19 lists the results obtained when the Niax PPG-2025-Hylene TM-65 prepolymer was reacted with various amines in JP-4. The products obtained ranged from a thick slurry to a precipitate, but no gels were obtained.

In Table 18 it is shown that the Niax PPG-1025-Hylene TM-65 prepolymer when reacted with amines such as Alamine 4D (lauryl amine) or Alamine 21D (Coco primary amine) produced a weak gel in JP-4 at concentrations ranging from 1.7 to 3.4 weight percent additive. In view of these findings, the possibility existed that the introduction of a trifunctional compound into the prepolymer would give rise to crosslinking, which might increase the rigidity of the gel. As a result, a prepolymer which consisted of Niax PPG-1025, glycerol and Hylene TM-65 was prepared. The purpose of the glycerol was to provide sites for crosslinking. This prepolymer was then evaluated with several amines in the presence of jet fuel. The results of this evaluation are listed in Table 20. In run number 3-38-6, the reaction of lauryl amine with the prepolymer gave a

voluminous precipitate, whereas when the polymer did not contain glycerol (Table 18, run number 2-38-1), a weak gel was obtained. These experiments indicated that if the proper triol was used in the terpolymer, the possibility existed that a satisfactory gelling system could be developed.

As a result of the above findings, various triols were reacted with Hylene TM-65 in order to determine their characteristics in JP-4. The results are listed in Table 21. The triols used (Pluracols as supplied by Wyandotte Chemical Corp.) are polyoxypropylene adducts of trimethylolpropane. It may be observed that all of the adducts are soluble in JP-4, even in concentrations as high as 6.1 weight percent. Because of the solubility of these products in JP-4, the possibility existed that a good gel could be obtained by preparing prepolymers containing various percentages of the triol with those diol-Hylene TM-65 adducts that formed precipitates when reacted with various amines in JP-4.

It was previously stated that many of the commercially available poly(propylene glycols) and poly(ethylene glycols) are insoluble in JP-4. It was also found that the isocyanate-terminated prepolymers prepared from these glycols were insoluble in JP-4. As a result, a series of modified polyalkylene glycols were evaluated in an effort to obtain an increased solubility in JP-4. The glycols considered were ethylene oxide and propylene oxide adducts of fatty amines. They are commercially manufactured by Armour Chemical Company under the trade names of "Ethomeen" and "Propomeen". In order to initiate this study, the characteristics of the various Ethomeens were evaluated by reaction with Hylene TM-65 in the presence of JP-4. The results of these evaluations are listed in Table 22. On examination of the results, it can be noticed that the majority of the Ethomeen-Hylene TM-65 products were either soluble or partially soluble in JP-4. This high solubility in jet fuel was to be expected, since the Ethomeen-Hylene TM-65 adducts contain long alkyl side-chains. It was thought that reacting various blends of Ethomeens and poly(propylene glycols) with an excess of Hylene TM-65 would yield prepolymers that were soluble in JP-4. The prepolymers could then be reacted with various amines in the fuel.

In order to complete the evaluation of the polyalkylene oxide adducts of fatty amines, the Propomeens were evaluated. The Propomeens studied were Propomeen C/12, C/25, HT/12, and HT/25. The various Propomeens were reacted with Hylene TM-65 in JP-4 by using a mixture of water, n-methyl morpholine, triethyl amine, and stannous octoate as the catalyst. The results are listed

in Table 23. It may be observed that the C/12 and HT/12 Propomeens yielded products that were soluble in JP-4, whereas the C/25 adduct produced a flocculent precipitate.

The next series of experiments utilizing the Propomeens was the preparation of a prepolymer by reacting the Propomeens with an excess of tolylene diisocyanate. The prepolymer could then be reacted with various amines in an attempt to gel JP-4. Several attempts were made to prepare the prepolymers; however, with all four of the Propomeens, after approximately one-half of the diisocyanate was added, the reaction mixture foamed, forming a hard, insoluble polymer. The possibility existed that the Propomeens were contaminated with water. As a result, an attempt was made to remove any water present by azeotroping it with toluene. This, however, failed to stop the Propomeens from forming an insoluble resin by reaction with tolylene diisocyanate. The next attempt to purify the Propomeens was to distill them. The Propomeens C/12 and HT/12 were distilled; the C/25 and HT/25 could not be distilled due to their high boiling points. Efforts to steam distill the C/25 and HT/25 also failed. The next approach to purify the C/25 and HT/25 was to wash the Propomeen with water containing HCl. The purpose of this was to remove any residual alkali catalyst that might be present in the Propomeen. The water was removed by azeotroping it with toluene. The material was decolorized by using Norit A (activated carbon) and the toluene removed under vacuum. This treatment likewise failed to prevent foaming and solidification when attempts were made to prepare the Propomeen-diisocyanate adduct.

The distilled HT/12 and C/12 were reacted with an excess of tolylene diisocyanate to prepare a prepolymer soluble in JP-4. These prepolymers were then reacted with various amines in the presence of JP-4. The results of the HT/12-tolylene diisocyanate (Nacconate 80, 80 weight percent 2, 4-isomer and 20 weight percent 2, 6-isomer) adducts are listed in Table 24. It may be observed that soluble products were obtained when the adduct was reacted with substituted 1,3-propylene diamines. With methane diamine, the adduct produced a precipitate. With the various fatty amines, the adduct produced either a thin gel or a soluble product in JP-4. As a result of these tests, Propomeen C/12 appears to be a promising material to blend with various propylene glycols before reacting it with diisocyanates in order to obtain a prepolymer soluble in JP-4.

The results of the Propomeen C/12-diisocyanate adduct are listed in Table 25. It is of interest to note that this adduct, when reacted with substituted 1, 3-propylene diamines, produced flocculent

precipitates that were approaching a gel in JP-4. It was previously stated that the HT/12 adduct produced a soluble product when reacted with the same amines. Table 25 also shows that the C/12-diisocyanate adduct, when reacted with various fatty amines, produced products that ranged from being soluble in JP-4, as shown with Armeen 18, to being a precipitate as was obtained when reacted with Alamine 21D. If the results obtained with the Propomeen C/12-diisocyanate adduct are compared with the results obtained with the Propomeen HT/12-diisocyanate adduct, as is done in Tables 24 and 25, it may be observed that, in general, the Propomeen C/12-diisocyanate adduct forms a flocculent precipitate which approaches a gel in JP-4 when reacted with substituted propylene diamines; whereas the Propomeen HT/12-diisocyanate adduct forms a soluble product with the same amines. With the primary fatty amines, the opposite is observed in that the Propomeen C/12-diisocyanate adduct produces a soluble product in JP-4, and the Propomeen HT/12-diisocyanate produces a thin gel when reacted with the same amines.

In order to evaluate further Propomeen HT/12, two prepolymers were prepared, using a diol or triol with the Propomeen and the diisocyanate. One prepolymer was prepared by reacting 0.1 mole Propomeen HT/12 and 0.05 mole of Niox 150 [a poly(propylene glycol) with an average molecular weight of 150] with 0.33 mole of Hylene TM-65. The resulting prepolymer had a NCO equivalent of 0.0032 eq/gm. The second prepolymer consisted of 0.1 mole Propomeen HT/12, 0.017 mole of Niox LG-168 (a triol having an average molecular weight of 1000), and 0.38 mole of Hylene TM-65. This prepolymer had a NCO equivalent of 0.0037 eq/gm. Attempts were made to gel JP-4 by reacting the afore-mentioned prepolymers with various amines. The results of these tests are listed in Table 26. These results indicate that although gels were obtained in all cases, the most promising was the one obtained from the prepolymer containing the triol. In view of the above results, the possibility exists that a superior gel could be obtained by selecting the proper diol or triol, preparing a prepolymer with the Propomeen and Hylene TM-65, and subsequently reacting the prepolymer with an amine.

ATTEMPTED FUEL GELATION BY USING VARIOUS ISOCYANATES AND ACIDS

During the course of investigating various diisocyanate prepolymers as potential agents in the solidification of fuels, amines were used as the coreactant in the majority of the tests since they are known to react very rapidly with the isocyanate group. However, acid

groups will also rapidly react with isocyanates in the presence of suitable catalysts. Table 27 lists the results obtained when various acids were reacted with Hylene TM-65 as well as with a prepolymer containing free isocyanate groups. The catalyst in all cases was a 70:30 mixture of cobalt naphthenate and N-methylmorpholine. It may be observed in run number 3-9-2 that a dimer acid (Empol 1014) was reacted with the Niox 1025-Hylene TM-65 prepolymer to produce a product soluble in JP-4. When treated with Hylene TM-65, the same acid produced a voluminous precipitate with the evolution of carbon dioxide. Of the various acids tested, not one produced a gel when it was reacted with an isocyanate in jet fuel. Another disadvantage of the acid-isocyanate system is that the rate of reaction is too slow to warrant further investigation.

POLYACRYLATES AND POLYMETHACRYLATES AS FUEL GELLING AGENTS

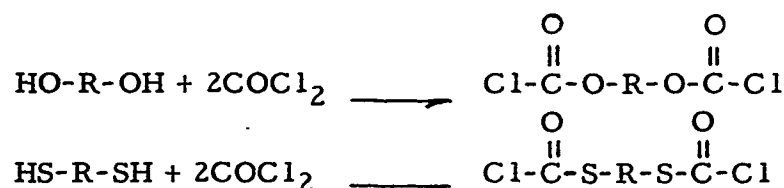
Other polymer systems investigated during the course of this program were the polyacrylates and polymethacrylates. Many of these polymers are hydrocarbon-soluble, and with some modification to produce reactive sites for crosslinking, they should offer a potential gelling system for jet fuels. The polymer used to initiate this investigation was "Lucite" 45 (isobutyl methacrylate polymer). This polymer is a commercially-available resin manufactured by Du Pont. The technique used was to heat a mixture of the resin and KOH in decanol at 190°C for 16 to 20 hours. In the two experiments made, the hydrolyzed resins had an acid number of 0.65 and 0.52. These resins were then reacted with tetrabutyl titanate in JP-4. In run numbers 4-1-1 and 4-1-2 listed in Table 28, it may be observed that the resin "oiled out" of the JP-4 in the form of a highly viscous fluid.

While the above hydrolysis reactions were being completed, a series of polymerization reactions were made in order to make a tailor-made polymer that would gel fuel. The monomers were 2-ethylhexyl acrylate and acrylic acid. A solution polymerization and an emulsion polymerization were made in order to vary the molecular weight. The emulsion polymerization yielded a polymer insoluble in JP-4 due to its high molecular weight. The solution polymerization yielded a polymer soluble in JP-4 and had an acid number of 0.50. In run number 4-1-3 listed in Table 28, the polymer was reacted with tetrabutyl titanate. By the use of a concentration of 4.7 weight percent additives, an elastic gel was obtained that could be stretched like a piece of rubber. This was undoubtedly the best gel obtained to date, and it certainly had enough rigidity to meet the desired specifications. But this system presented two problems that practically

eliminate it as a potential gelling system. The first problem is that the resin is a solid. As a result, it has to be dissolved in JP-4 prior to injection into the fuel. The second disadvantage is that the rate of reaction is slow; the system had to be agitated after the reactants were injected. This system offers an excellent possibility of producing a strong gel. It is thought that by further modification of the acrylate polymers and by the use of more reactive organo-titanates or other organo-metallics, the rate of gelation could be significantly increased. The use of organo-metallics is attractive, since in this way polymers might be formed that have a certain degree of fire retardance.

CHLOROFORMATES AS FUEL GELLING AGENTS

It was previously reported that the most promising rapidly-forming gel obtained to date is not polymeric in nature, since it is the reaction product of a diisocyanate and a mono-amine. In an effort to evaluate other rapidly-reacting systems, attention was directed toward the chloroformates and thiolchloroformates. These materials are synthesized by reacting the corresponding alcohol or thiol with phosgene. The general reactions are listed as follows:



Since this work was done immediately prior to the end of the program, time permitted the evaluation of only one chloroformate. This compound, n-propylthiolchloroformate, was supplied by Stauffer Chemical Company. The n-propylthiolchloroformate was reacted with various amines in the presence of JP-4. The results are listed in Table 29. In run number 5-25-3, it may be observed that a gel was obtained when n-propylthiolchloroformate was reacted with Alamine 21D (Coco amine) in the presence of JP-4.

It is believed that the chloroformate-amine system is worthy of further investigation, since this system can be modified with various side groups in order to vary its solubility in jet fuel. With the development of the proper modified dichloroformate, it could be reacted with a diol or diamine. The structure would be polymeric in nature; therefore the gel rigidity would be increased.

FUEL GEL EVALUATION

With respect to the gelation of jet fuels, it is understood that the ultimate goal of the research is to obtain the strongest gel in the shortest period of time with the minimum quantity of additives. During the course of this program, several systems that would rapidly gel fuels were developed. Efforts were directed toward those systems that would produce a firm gel by using from 1 to 4 weight percent additives. Generally speaking, the rigidity of a gel can be increased by increasing the amount of additives; however, an increase in the amount of additives would also increase the weight penalty. Therefore, in this line of thinking, some effort was directed toward evaluating various properties of the gels in order to obtain preliminary information with respect to the suitability of the gelling system when utilized in a plane crash.

BENCH-SCALE INJECTION EQUIPMENT

While a chemical system that will solidify JP-4 was being developed, a simultaneous program was initiated in which various injection techniques were investigated in order to evaluate the feasibility of utilizing the chemical systems that were being considered. Figure 1 shows the bench scale equipment that was used to investigate injection patterns as well as gelling tests. The container, measuring 5-1/2" X 5-1/2" X 10", is made of Plexiglas. One gallon of JP-4 is used per test. The injection system consists of a copper tube with multiple orifices. The tube containing the orifices was designed so that (1) complete injection could be accomplished in 2 seconds; (2) there could be approximately 10-psi pressure drop in the line and orifices; and (3) 16 orifices could be used along the length of the tube. It was calculated that 1/8-inch tubing with 1/16-inch orifices would satisfy all conditions, including the 10-psi pressure drop, necessary to inject an equivalent of 4 percent of reactants into one gallon of fuel. In order to evaluate the injection system, octadecyl amine was dissolved in the fuel. A dyed diisocyanate solution was then injected into the tank, and the injection pattern was observed with a high speed camera.

Several pictures were taken in order to illustrate the amine-diisocyanate system. The technique employed was to introduce octadecyl amine into the fuel. This may be observed in Figure 1. At zero time the tolylene diisocyanate was injected into the fuel by using the injection system as described above. A total of 4 weight percent additives based on the fuel were used in this experiment. Figure 2 shows the gelled fuel 55 seconds after the tolylene diisocyanate had been



injected. However, the fuel had gelled shortly after the diisocyanate had been injected. If the container is observed closely near the top, entrapped air bubbles may be seen. This shows that the fuel had gelled before all the air bubbles had escaped, indicating that a rapid reaction had occurred.

Figure 3 shows the gel after it had been removed from the container. Figure 4 shows the gel after being cut into small pieces. A high-speed movie was made of this experiment; this better shows the mixing of the reagents as well as the properties of the gel. This movie has been submitted to the Sponsor.

DETERMINATION OF HEAT OF REACTION FOR THE LAURYL AMINE-HYLENE TM-65 REACTION

While the use of the lauryl amine-tolylene diisocyanate reaction as a means for gelling fuel was being investigated, experiments had shown that the fuel could be gelled with as low as one weight percent additive. If, for example, a charge of two weight percent additives based on a full fuel load is installed in a plane, this concentration will gradually increase during the flight due to fuel consumption. Since the amine-diisocyanate reaction is exothermic, a series of tests were made in which the concentration of the adduct was increased. This would simulate what would occur during flight. The test was made by adding the reactants to the fuel in a Dewar flask. The temperature increase was measured by a thermometer submerged in the gel. A plot of weight percent additive versus temperature increase is shown in Figure 5. It may be observed that the temperature increases quite rapidly with concentration. At higher concentrations the theoretical temperature increase may be somewhat higher than the plot shows. The reason for this is that at these high concentrations, the fuel is converted to a hard solid and is crumbled into small pieces before complete mixing of the reactants can be obtained.

EFFECT OF GELATION ON THE VAPOR PRESSURE OF FUELS

It is known that, in a plane crash, one of the greatest fire hazards is fuel misting. This occurs when a tank is ruptured and when the fuel, as it drains from the tank, is atomized by the high velocity air. The atomized fuel rapidly reaches its explosive limits and is readily ignited by a spark or hot spot. The possibility exists that if a large hole is torn in the tank, the gelled fuel might be extruded through the hole by the force of impact or by the high velocity air. Laboratory tests made on the gels prepared during this program showed that the gels can be broken into pieces by impact or by a high velocity air stream; however, the gel will not atomize.

It was of interest to determine what effects the gel would have on the vapor pressure of the fuel, since this would give some indication of the effectiveness of the gel. In order to make this determination, gasoline was used as the fuel, since it has a much higher vapor pressure than jet fuel. Reid Vapor Pressure equipment was used to determine the vapor pressures. The only modification to the standard procedure was that the fuels were not agitated. The plots of vapor pressure versus time for regular gasoline and gelled gasoline are shown in Figure 6. The real significance of these plots is shown in the first few minutes, since it is this period which is of interest in case of a plane crash. One can observe that the gel has significantly reduced the vapor pressure of gasoline even for several hours. It was previously stated that the gelled fuel will not atomize, and since the gelation process greatly decreases the vapor pressure of the fuel, it must be concluded that the fuel gel will significantly decrease the potential fire hazard in plane crashes.

EXPERIMENTATION

The following is a list of the various compounds and prepolymers synthesized during the course of this program.

REACTION OF MENTHANE DIAMINE AND DIMER ACID

A mixture of 34.0 grams (0.3 mole) menthane diamine and 25.0 grams xylene was placed in a flask equipped with a stirrer, thermometer, dropping funnel, condenser and water-trap. After heating the mixture to 60°C, a solution of 30.0 grams (0.1 mole) dimer acid (Empol 1014) in 25.0 grams xylene was added by drops. The temperature was slowly raised to 190°C, during which time the xylene and water were removed from the water-trap. The temperature was then raised to 260°C and held at that temperature for 0.5 hour. The material was then cooled and used in the fuel gelation study.

REACTION OF PRIMENE JM-T AND DIMER ACID

A mixture of 8.5 grams (0.021 mole) Primene JM-T (Rohm & Haas) and 10 grams of xylene was heated to 60°C, and a solution of 3.0 grams dimer acid (Empol 1014) in 10 grams xylene was added by drops. The mixture was then heated to 160°C in order to remove the xylene and the water formed. The temperature was then slowly raised to 290°C and held at this temperature for 0.5 hour. The material was then cooled and used in the fuel gelation study.

REACTION OF ARMEEN 12 AND MENTHANE DIAMINE WITH DODECENYL SUCCINIC ANHYDRIDE

A mixture of 2.7 grams (0.01 mole) dodecenyl succinic anhydride, 1.8 grams (0.01 mole) Armeen 12 (mainly dodecyl amine), and 25 grams JP-4 was heated at 60°C for 15 minutes. Then 1.7 grams (0.01 mole) menthane diamine (Rohm & Haas) was added and the heating continued for an additional 15 minutes.

CYANOETHYLATION OF POLY(PROPYLENE GLYCOL)

In a flask equipped with a thermometer, stirrer, dropping funnel, and condenser were placed 300.0 grams (2.0 moles) poly(propylene glycol) PPG-150 (molecular weight 150), 6.0 grams of a 25 weight percent aqueous solution of Triton B, and 6.0 grams of hydroquinone. The mixture was heated to 80°C in order to obtain a homogeneous solution.



After cooling the solution to 15°C, 228.0 grams (4.30 moles) of acrylonitrile was added by drops, maintaining the temperature between 15-25°C. After the addition of acrylonitrile was completed, the mixture was stirred at room temperature for 6 hours. The temperature was then raised to 50°C, and stirring was continued for an additional 2 hours. The mixture was then diluted with 200 ml water, acidified with hydrochloric acid, and extracted with ethylene dichloride. The organic layer was separated, dried, and the solvent removed by distillation.

REDUCTION OF DICYANOETHYL ADDUCT OF POLY(PROPYLENE GLYCOL)

In a round-bottom flask equipped with a thermometer, stirrer, dropping funnel, condenser, and a nitrogen sweep gas system were placed 1300.0 ml anhydrous ether and 49.4 grams (1.3 moles) of lithium aluminum hydride. The mixture was heated to reflux in order to dissolve the hydride and then cooled to 10°C; 190.0 grams (0.65 mole) of the dicyanoethyl adduct of poly(propylene glycol) dissolved in 180 ml of ether was added by drops, while a temperature between 20 to 25°C was maintained. The mixture was stirred for one hour after the addition was complete. To the mixture was successively added 52.0 ml water, 39.0 ml 20 weight percent aqueous sodium hydroxide, and finally 150.0 ml water. The organic layer was separated from the solids and dried over sodium sulfate. The solvents were removed by vacuum distillation, and the crude product was used in the fuel gel evaluation.

PREPARATION OF p-PHENYLENE DIISOCYANATE

A mixture consisting of 181.0 grams (1.0 mole) p-phenylene diamine dihydrochloride, 860 ml xylene, and 140 ml o-dichlorobenzene was placed in a flask equipped with a gas dispersion tube, thermometer, nitrogen inlet, stirrer, and condenser. The system was swept with nitrogen for 15 minutes. Phosgene was bubbled into the rapidly-stirred suspension, and the temperature was raised to reflux (140-142°C). The phosgenation reaction was continued for 12 hours, after which time the mixture was cooled to room temperature. The solids were removed by filtration, and the solvents were distilled off under vacuum. Then the crude p-phenylene diisocyanate was recrystallized from hot hexane. The melting point was 92 to 94°C.

PREPARATION OF 2,6-TOLUENEDIAMINE DIHYDROCHLORIDE

A mixture consisting of 200.0 grams (1.05 moles) 2,6-dinitrotoluene, 363.0 grams (6.6 moles) powdered iron, and 440.0 ml aqueous

ethanol (50 weight percent) was heated to boiling, and a solution containing 22.9 ml (0.264 mole) of concentrated hydrochloric acid in 110 ml of a 50-weight percent solution of ethanol in water was added by drops. The mixture was refluxed for two hours after the addition of the acid. After the reflux time was completed, the apparatus was disconnected, and the hot mixture was made alkaline to litmus by the addition of 127 ml of a 15-weight percent solution of alcoholic potassium hydroxide. The hot mixture was then filtered to remove the excess iron, and the flask was washed with two 200.0-ml portions of 95 weight percent ethanol. The same alcohol was used to wash the iron. To the filtrate was added 370.0 ml of 6.0 N. hydrochloric acid. The mixture was cooled to 25°C and filtered by suction. The product was washed with two 100.0-ml portions of 95 weight percent ethanol and dried in a vacuum dessicator.

PREPARATION OF 2,6-TOLYLENE DIISOCYANATE

The crude 2,6-toluene-diamine dihydrochloride, 860 ml xylene, and 140 ml o-dichlorobenzene were placed in a round-bottom flask equipped with a gas dispersion tube, thermometer, nitrogen inlet, stirrer, and condenser. The system was swept with nitrogen for 15 minutes. Phosgene was bubbled into the rapidly-stirred suspension, and the temperature was raised to 135°C. The phosgenation reaction was continued for 7.5 hours, at which time all of the solids had gone into solution. The pure 2,6-tolyene diisocyanate was obtained by fractional distillation. The boiling point was 128°C at 15 mm mercury.

PREPARATION OF N-LAURYL-DIETHYLENE TRIAMINE

A mixture consisting of 186.0 grams (1.0 mole) lauryl alcohol, 205.0 grams (1.0 mole) lauryl chloride, and 89.0 grams (1.0 mole) diethylene triamine was heated under reflux for 0.5 hour. Then 44.5 grams (0.5 mole) diethylene triamine was added, and the reflux was continued for an additional 0.5 hour. After cooling the mixture to 100°C, a solution of 40.0 grams (1.0 mole) NaOH dissolved in 40.0 grams water was added. The solution was again heated under reflux for 0.5 hour. After cooling, the product was diluted with 100 grams of JP-4 and the insoluble salts removed by filtration. The low boiling materials were stripped under a vacuum of 1 mm Hg to a pot temperature of 230°C and a head temperature of 150°C. The crude N-lauryl-diethylene triamine was used in the fuel gel evaluation.

REACTION OF POLYBUTADIENE-ACRYLIC ACID COPOLYMER WITH TRIETHYLENETETRAMINE

In a flask equipped with a thermometer, condenser, and water trap were placed 36.5 grams triethylenetetramine, 28.0 grams polybutadiene-acrylic acid copolymer, and 125 grams of mineral spirits. The temperature was slowly raised to 160°C and held there for 7 hours. The mineral spirits was removed under vacuum, and the crude modified copolymer was used in the fuel gelation study.

PREPARATION OF POLY(PROPYLENE GLYCOL)-HYLENE TM-65 PREPOLYMERS

The equipment used in this experiment was a round-bottom flask equipped with a stirrer, thermometer, dropping funnel, condenser, and nitrogen inlet tube. After the system was swept with nitrogen, 184.0 grams (2.12 equivalents) of Hylene TM-65 was added and heated to 60°C. Then a mixture of 521.0 grams (1.0 equivalent) of poly(propylene glycol) PPG-1025 and 0.6 grams N-methylmorpholine was slowly added to the diisocyanate. The solution was then heated for 2.0 hours at 125°C. The prepolymer was stored under nitrogen until it was evaluated.

The poly(propylene glycol) PPG-2025-Hylene TM-65 prepolymer was prepared in an identical manner, maintaining the same equivalent ratios.

PREPARATION OF PROPOMEEN C/12-NACCONATE 80 PREPOLYMER

To a dry, nitrogen-purged flask equipped with a stirrer, thermometer, condenser, dropping funnel, and a nitrogen sweep gas system were charged 81.0 grams (0.25 mole) Propomeen C/12, 100.0 grams of dry JP-4, and 0.25 grams of N-methylmorpholine. The mixture was heated to 50°C, and 96.0 grams (0.55 mole) Nacconate 80 was slowly added, while a temperature of 70°C was maintained. After the addition was complete, the mixture was held at 70°C for 4 additional hours. The cooled prepolymer was stored under nitrogen until evaluated.

PREPARATION OF PROPOMEEN HT/12-NACCONATE 80 PREPOLYMER

To a dry, nitrogen-purged flask equipped with a stirrer, thermometer, condenser, dropping funnel, and a nitrogen sweep gas system were added 128.0 grams (0.30 mole) Propomeen HT/12, 0.25 grams N-methylmorpholine, and 100.0 grams of dry JP-4. The mixture was heated to

50°C, and 128.0 grams (0.75 mole) of Nacconate 80 was slowly added, while a temperature of 70°C was maintained. After the addition was complete, the mixture was held at 70°C for 3 additional hours. The cooled prepolymer was stored under nitrogen until evaluated.

PREPARATION OF POLY(PROPYLENE GLYCOL) PPG-1025-HYLENE TM-65-GLYCEROL PREPOLYMER

To a dry, nitrogen-purged flask were added 205.0 grams (0.2 mole) Niox PPG-1025, 1.8 grams (0.02 mole) dry glycerol, and 0.6 grams N-methylmorpholine. The mixture was heated to 80°C, and 80.0 grams (0.46 mole) Hylene TM-65 was slowly added. After the addition was completed, the solution was heated to 125°C for 0.5 hour and then cooled to room temperature. The prepolymer was stored under nitrogen until evaluated.

PREPARATION OF PROPOMEEN HT/12-NIAX PPG-150-TM-65 PREPOLYMER

The equipment was a 1-liter resin pot equipped with a thermometer, dropping funnel, stirrer, condenser, and nitrogen-sweep gas system. After the system was purged with nitrogen, the flask was charged with 37.4 grams (0.215 mole) Hylene TM-65 and 101.5 grams of JP-4. After the solution was heated to 50°C, 36.5 grams (0.1 mole) of Propomeen HT/12 was slowly added, followed by the addition of 7.5 grams (0.05 mole) of poly(propylene glycol) Niox PPG-150. Finally 20.0 grams (0.115 mole) of Hylene TM-65 was added, and the temperature was held at 60°C for an additional hour. The cooled prepolymer was stored under nitrogen.

Analysis:

4.0 grams of the polymer solution were diluted with 25.0 grams toluene and reacted with 50.0 ml of a 0.143 normal solution of n-butylamine in toluene followed by the addition of 50.0 ml isopropanol. Four drops of bromophenol blue was added and the solution titrated with 0.1 normal HCl.

Equivalent NCO/gram sample = 0.0032.

PREPARATION OF PROPOMEEN HT/12-NIAX TRIOL LG-168-HYLENE TM-65 PREPOLYMER

The equipment was a 1-liter resin pot equipped with a thermometer, dropping funnel, stirrer, condenser, and nitrogen-sweep gas system. After the system was purged with nitrogen, the flask was charged with 37.4 grams (0.215 mole) Hylene TM-65 and 127.0 grams of JP-4. After the solution was heated to 50°C, 36.5 grams (0.1 mole) of Propomeen HT/12 was slowly added, followed by the addition of 33.0 grams (0.017 mole) Niaux Triol LG-168. Finally, 30.0 grams (0.172 mole) of Hylene TM-65 was added, and the temperature was held at 60°C for an additional hour. The cooled prepolymer was stored under nitrogen.

Analysis:

4.0 grams of the polymer solution were diluted with 25.0 grams toluene and reacted with 50.0 ml of a 0.143 normal solution of n-butylamine in toluene followed by the addition of 50.0 ml isopropanol. Four drops of bromophenol blue was added and the solution titrated with 0.1 normal HCl.

Equivalent NCO/gram sample = 0.0037.

HYDROLYSIS OF POLY(ISOBUTYL METHACRYLATE)

In a round-bottom flask equipped with a stirrer, thermometer, and condenser were placed 250.0 grams decanol, 80.0 grams poly(isobutyl methacrylate) ("Lucite 45" as manufactured by Du Pont), and 9.0 grams potassium hydroxide. The mixture was heated, with stirring, for 16.0 hours at 190°C. The cooled solution was then diluted with 150.0 ml butanol, followed by the addition of 20.0 ml concentrated hydrochloric acid. The mixture was then heated under reflux for an additional 1.5 hours. On cooling, the solution was water washed to remove the potassium chloride, and the solvents were removed under vacuum. The polymer was purified by dissolving it in an equal volume mixture of methyl ethyl ketone, acetone, and dimethyl formamide followed by precipitation in water.

Analysis:

2.0 grams of the hydrolyzed polymer were dissolved in 50.0 ml acetone and titrated with 0.1 normal potassium hydroxide using phenolphthalein as the indicator.

Acid No. = 0.65.

PREPARATION OF 2-ETHYLHEXYL ACRYLATE AND ACRYLIC ACID COPOLYMER BY SOLUTION POLYMERIZATION

In a resin pot equipped with a dropping funnel, stirrer, thermometer, condenser, and nitrogen-sweep system was placed 280.0 grams of dried JP-4. The jet fuel was heated to 60°C, and a mixture of 92.0 grams (0.5 mole) 2-ethylhexyl acrylate and 7.2 grams (0.1 mole) acrylic acid was rapidly added to the flask, followed by the addition of 0.8 gram benzoyl peroxide and 1.25 grams t-dodecyl mercaptan in 5.0 grams benzene. The temperature was then raised to 90°C and held there for 4.0 hours. This solution was used in the fuel gel evaluation.

Analysis:

10.0 grams of the polymer solution (containing 2.42 grams of the polymer) were added to 50.0 ml. of acetone, and the acid groups on the polymer were titrated with 0.1 normal potassium hydroxide, with phenolphthalein being used as the indicator.

Acid No. = 0.50.

APPENDIX I

TABLE 1
SMA HALF-ESTERS WITH AMINES AND DIISOCYANATES

| Run No. | Wt % Half-Ester | Amine | Wt % Amine | Wt% Toluene-Diisocyanate | Wt % Additive | Wt % Fuel | Results |
|---------|-------------------------|---------------------|------------|--------------------------|---------------|-----------|--|
| I-18A | 2.65 (C ₈) | Diethylene-Triamine | 3.0 | 12.0 | 17.65 | 82.35 | Produced a firm, dry gel. |
| I-19A | 2.64 (C ₈) | Diethylene-Triamine | 1.5 | 7.4 | 11.3 | 88.7 | Thick slurry, additional diisocyanate produced a firm gel. |
| I-21-1 | 5.82 (C ₁₂) | Diethylene-Triamine | 0.4 | 2.5 | 8.72 | 91.28 | Thick slurry, gelled in 45 min. |
| I-21-3 | 2.5 (C ₁₂) | Ethylene Diamine | 2.0 | 4.0 | 8.5 | 91.5 | Thick slurry, gelled in 30 min. |
| I-26-1 | 0.95 (C ₁₂) | Ethylene Diamine | 3.77 | 5.65 | 10.46 | 90.54 | Firm, dry gel in 30 sec. |
| I-26-3 | 2.0 (C ₁₂) | Ethylene Diamine | 2.5 | 5.0 | 9.5 | 90.5 | Thin slurry. |

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TABLE 2
JP-4 GELATION BY USING VARIOUS AMINES AND DIBASIC ACID CHLORIDES

| Run No. | Amine | | Acid Chloride | | Wt % | | Results |
|---------|---|------|---------------|------|-------|-----------------|----------------------------------|
| | Name | Wt % | Name | Wt % | Water | Total Additives | |
| 3-1-1 | Diam-21 (N-Coco 1, 3-propylene diamine) | 1.38 | Sebacoyl | 1.2 | 0.5 | 3.08 | Flocculent suspension. |
| 3-2-7 | " " | 1.38 | Phthaloyl | 1.2 | 0.5 | 3.08 | Slight thickening of fuel. |
| 3-1-2 | Diam-26 (N-Tallow-1, 3-propylene diamine) | 1.82 | Sebacoyl | 1.2 | 0.5 | 3.52 | Flocculent suspension. |
| 3-2-8 | " " | 1.82 | Phthaloyl | 1.2 | 0.5 | 3.52 | Slight thickening of fuel. |
| 3-1-4 | Alamine-4D (Lauryl amine) | 1.89 | Sebacoyl | 0.6 | 0.5 | 2.99 | Heavy suspension of white solid. |
| 3-2-10 | " " | 1.89 | Phthaloyl | 0.6 | 0.5 | 2.99 | Product soluble in fuel. |
| 3-1-5 | Alamine 21D (Coco amine) | 2.0 | Sebacoyl | 0.6 | 0.5 | 3.1 | Thin gel. |
| 3-2-11 | " " | 2.0 | Phthaloyl | 0.6 | 0.5 | 3.1 | Slight thickening of fuel. |

TABLE 3
MODIFIED DIMER ACID - AMIDES AS GELLING AGENTS

| Run No. | Type of Modified Dimer Acid | Compound B | | Compound C | | Wt % Total Additives | Results |
|---------|-----------------------------|------------|-------------------|------------|---|----------------------|-----------------------|
| | | Wt % | | Wt % | | | |
| 2-5-4 | A* | 3.1 | Sebacoyl Chloride | 2.5 | - | 5.6 | Thick slurry, no gel. |
| 2-9-2 | B** | 14.6 | Sebacoyl Chloride | 9.8 | - | 24.4 | Ppt. |
| 2-11-2 | C*** | 2.0 | Sebacoyl Chloride | 1.0 | - | 3.0 | Flocculent ppt. |

*Armeen 12, menthane diamine amide of dodecenyl succinic anhydride.
 **Primene JM-T (Rohm & Haas) amide of Empol 1014 (Emery Industries).
 ***Menthane diamine amide of Empol 1014.

TABLE 4
ATTEMPTED SOLIDIFICATION OF JP-4 BY USING VARIOUS EPOXIDE POLYMERS

| Run No. | Epoxide | Wt % | Curing Agent | Wt % | | Results |
|---------|-------------------------------------|------|------------------------|------|-----------------|-----------------------------|
| | | | | Wt % | Total Additives | |
| 3-3-1 | Oxiron-2001 (Food Machinery) | 3.0 | Tri-m, p-cresyl borate | 1.0 | 4.0 | Heavy ppt., rapidly formed. |
| 3-3-2 | Araldite-506 (Ciba) | 3.0 | Tri-m, p-cresyl borate | 1.0 | 4.0 | Fine ppt. |
| 3-3-3 | Unox Epoxide 201 (Union Carbide) | 3.0 | Tri-m, p-cresyl borate | 1.0 | 4.0 | Heavy suspension. |
| 3-3-4 | Unox Epoxide 201 (Union Carbide) | 3.0 | EM-550 (Thiokol) | 1.0 | 4.0 | EM-550 Insoluble in JP-4. |
| 3-3-5 | Epoxy X-71 (Shell Chemical) | 3.0 | Tri-m, p-cresyl borate | 1.0 | 4.0 | Voluminous ppt. |

TABLE 5
ATTEMPTED SOLIDIFICATION OF JP-4 BY USING VARIOUS EPOXIDES

| Run No. | Epoxide | Wt % | Coreactant | Wt % | Wt % Catalyst | Wt % Total Additives | Results |
|---------|---|------|---|------------|----------------------|----------------------|--|
| 3-8-1 | Unox 206 (vinylcyclohexene diepoxide) | 5 | Tri-m, p-cresyl borate | 1.0 | - | 6.0 | Formed a gummy ppt. |
| 3-8-2 | Unox 269 (dipentene diepoxide) | 5 | Tri-m, p-cresyl borate | 1.0 | - | 6.0 | Soluble product. |
| 3-8-3 | Unox 269 | 2 | Niax Polyol L67 Tri-m, p-cresyl borate | 2.0 1.0 | - | 5.0 | Soluble product. |
| 3-8-5 | Unox 206 | 2 | Tri-m, p-cresyl borate Niax 1025 | 1.0 1.0 | - | 4.0 | Voluminous ppt. Agglomerated into a gummy mass. |
| 3-19-1 | Flexol PEP (di-(isodecyl) 4,5-Epoxy Tetrahydro-phthalate) | 4 | Tri-m, p-cresyl borate | 0.4 | - | 4.4 | Soluble product. |
| 3-19-2 | Flexol PEP | 4 | Tetramethyl guanidine | 1.0 | Stannous Octoate 0.1 | 5.1 | Soluble product. |

TABLE 5
ATTEMPTED SOLIDIFICATION OF JP-4 BY USING VARIOUS EPOXIDES (Cont'd)

| Run No. | Epoxide | Wt % | Coreactant | Wt % | Wt % Catalyst | Wt % Total Additives | Results |
|---------|--|------|--|---------|---------------|----------------------|------------------|
| 3-19-3 | Flexol EP-8 (epoxidized plasticizer) | 4 | Tri-m, p-cresyl borate | 0.5 | - | 4.5 | Soluble product. |
| 3-19-5 | Plastolein 9232 (epoxidized plasticizer) | 4 | Tri-m, p-cresyl borate | 1.0 | - | 5.0 | Flocculent ppt. |
| 3-20-9 | Plastolein 9214 (epoxidized plasticizer) | 3 | Dimer Acid 1014 Tri-m, p-cresyl borate | 2.0 0.5 | - | 5.5 | Slight ppt. |
| 3-21-12 | Flexol EP-8 | 3 | Dimer Acid 1014 Tri-m, p-cresyl borate | 2.0 0.5 | - | 5.5 | Slight ppt. |

TABLE 6
GELATION OF JP-4 WITH SUBSTITUTED POLYUREAS

| Run No. | Wt % Armeen 12* | Other Amines | Wt % | Hylene TM-65 Wt % | Total | | Results |
|---------|-----------------|--------------------|------|-------------------|---------------|-----------|--|
| | | | | | Wt % Additive | Wt % JP-4 | |
| 1-30-1 | 3.0 | - | - | 2.5 | 5.5 | 94.5 | Dry gel in few seconds. |
| 1-30-4 | 3.25 | - | - | 1.75 | 5.0 | 95.0 | Same as above. |
| 1-30-5 | 2.75 | - | - | 1.25 | 4.0 | 96.0 | Same as above. |
| 1-30-6 | 2.50 | - | - | 1.0 | 3.5 | 96.5 | Gelled rapidly. Gel broken by agitation. |
| 1-34-3 | 0.55 | - | - | 0.45 | 1.0 | 99.0 | Same as above. |
| 1-31-9 | 1.75 | Duomeen S** | 0.25 | 1.0 | 3.0 | 97.0 | Same as above. |
| 1-34-4 | 0.49 | Ethylene Diamine | 0.06 | 0.45 | 1.0 | 99.0 | Ppt. |
| 1-38-1 | 0.55 | Genamid 250*** | 0.55 | 0.45 | 1.55 | 98.45 | Suspended ppt.; poor gel. |
| 1-38-2 | 0.55 | Araldite DP-125† | 0.55 | 0.45 | 1.55 | 98.45 | Poor gel; fuel exuded. |
| 1-38-3 | 0.55 | Versamid†† XR-2000 | 0.55 | 0.45 | 1.55 | 98.45 | Suspended ppt.; no gel. |

*Armeen 12-(Armour); primarily dodecyl amine.

**Duomeen S-(Armour); primarily C18 diamine.

***Genamid 250-(General Mills); modified polyamine adducts.

†Ciba Araldite DP-125-(Ciba); modified polyamine hardener.

††Versamid XR-2000-(General Mills); modified polyamide.

TABLE 7
JP-4 GELATION BY USING VARIOUS AMINES AND HYLENE TM-65

| Run No. | Amine* | Wt % Amine | Wt % Hylene TM-65 | Wt % Total Additives | Results |
|---------|--|------------|-------------------|----------------------|---------------------------|
| 2-33-1 | Diam-21 (N-Coco-1,3-propylene diamine) | 1.4 | 0.43 | 1.83 | Solid suspension, no gel. |
| 2-33-2 | Diam-26 (N-Tallow-1,3-propylene diamine) | 1.44 | 0.35 | 1.79 | Soluble in JP-4. |
| 2-33-3 | Alamine 21D (Coco Amine) | 1.34 | 0.58 | 1.92 | Firm gel. |
| 2-33-4 | Diam-11 (N-Oleyl-1,3-propylene diamine) | 1.48 | 0.35 | 1.83 | Soluble in JP-4. |
| 2-34-5 | Alamine 11D (Oleyl Amine) | 1.38 | 0.43 | 1.81 | Weak gel. |
| 2-34-6 | Alamine 4D (Lauryl Amine) | 1.29 | 0.58 | 1.87 | Gel stronger than 2-34-5. |

*Amines are products of General Mills.

TABLE 8
MODIFICATION OF ARMEEN 12-TM-65 ADDUCT

| Run No. | Wt % | | Description Reactant 3 | Wt % | | Results |
|---------|------------|----------------|---------------------------|------------|-----------------|---|
| | Armeen 12* | Hylene TM-65** | | Reactant 3 | Total Additives | |
| I-39-1 | 0.55 | 0.45 | Vistanex 80*** | 1.0 | 2.0 | Weak gel. Inferior to amine TM-65 adduct. |
| I-39-2 | 0.55 | 0.45 | Butyl rubber-365† | 1.0 | 2.0 | Same as above. |
| I-42-2 | 0.33 | 0.33 | Modified PBA†† | 0.33 | 0.99 | Thick slurry; no gel. |
| I-40-1 | 0.55 | 0.23 | - | - | 0.78 | Better gel than I-34-1. |
| I-34-1 | 0.55 | 0.45 | - | - | 1.0 | Firm gel. |
| I-40-2 | 1.33 | 0.66 | - | - | 2.0 | Good gel. Better than above. |

* Mainly dodecyl amine (Armour).

**Tolylene diisocyanate (Du Pont).

***Polyisobutylene (Enjay).

†Butyl rubber (Enjay).

††Amide modified polybutadiene/acrylic acid (Thiokol).

TABLE 9
ATTEMPTS TO GEL JP-4 BY USING MODIFIED DIETHYLENE
TRIAMINES AND HYLENE TM-65

| Run No. | Modified Diethylene Triamine | Wt % | | Wt % | | Results |
|---------|-----------------------------------|-------|--------------|--------|-----------------|--|
| | | Amine | Hylene TM-65 | Hylene | Total Additives | |
| 2-35-1 | N-Lauryl diethylene triamine | 1.43 | 0.44 | 1.87 | | Slurry, no gel. Triamine slightly soluble in JP-4. |
| 2-35-3 | N-Oleoyl diethylene triamine | 1.47 | 0.35 | 1.82 | | Slurry, no gel. |
| 2-35-4 | N,N'-Di-oleyl diethylene triamine | 2.53 | 0.35 | 2.88 | | Adduct soluble in JP-4. |
| 2-35-5 | N-Lauryl diethylene triamine | 1.36 | 0.44 | 1.88 | | Adduct soluble in JP-4 |
| 2-31-1 | N-Octyl diethylene triamine | 1.56 | 0.44 | 2.0 | | Ppt. |

TABLE 10
ATTEMPTED FUEL GELATION BY USING PHENYL
ISOCYANATE AND VARIOUS AMINES

| Run No. | Amine | Wt % | Wt % | Wt % | Results |
|---------|---|-------|-------------------|-----------------|---|
| | | Amine | Phenyl Isocyanate | Total Additives | |
| 5-12-12 | Diam 21 (N-Coco-1, 3-propylene diamine) | 0.19 | 3.09 | 3.28 | Product soluble in fuel. |
| 5-12-13 | " " " | 1.12 | 2.88 | 4.0 | " " " |
| 5-12-14 | Diam 11 (N-Oleyl-1, 3-propylene diamine) | 1.11 | 2.89 | 4.0 | Formed slight ppt. |
| 5-12-15 | Diam 26 (N-Tallow-1, 3-propylene diamine) | 1.09 | 2.91 | 4.0 | " " " |
| 5-12-16 | Alamine 4D (Lauryl primary amine) | 1.86 | 2.14 | 4.0 | Formed a swollen ppt. but did not gel the fuel. |
| 5-13-18 | " " " | 1.14 | 2.86 | 4.0 | Product same as in run number 5-12-16. |
| 5-13-19 | Alamine 21D (Coco primary amine) | 1.18 | 2.82 | 4.0 | Product soluble in fuel. |
| 5-13-20 | Alamine 11D (Oleyl primary amine) | 1.45 | 2.55 | 4.0 | " " " |

TABLE II
ATTEMPTED FUEL GELATION BY USING m-TOLYL
ISOCYANATE AND VARIOUS AMINES

| Run No. | Amine | Wt % Amine | Wt % | | Results |
|---------|--|---------------|-----------------------|--------------------|--------------------------|
| | | | m-Tolyl Isocyanate | Total Additives | |
| 5-11-1 | Diam 21 (N-Coco-1, 3-propylene diamine) | 1.4 | 2.6 | 4.0 | Product soluble in fuel. |
| 5-11-3 | " " " " | 0.83 | 3.17 | 4.0 | " " " " |
| 5-11-4 | Diam 11 (N-Oleyl-1, 3-propylene diamine) | 1.02 | 2.98 | 4.0 | " " " " |
| 5-11-5 | Diam 26 (N-Tallow-1, 3-propylene diamine) | 1.0 | 3.0 | 4.0 | Formed slight ppt. |
| 5-11-6 | Alamine 4D (Lauryl primary amine) | 1.07 | 2.93 | 4.0 | " " " |
| 5-11-7 | Alamine 21D (Coco primary amine) | 1.09 | 2.91 | 4.0 | " " " |
| 5-11-8 | Alamine 11D (Oleyl primary amine) | 1.35 | 2.65 | 4.0 | Product soluble in fuel. |

TABLE 12
FUEL GELATION BY USING p-PHENYLENE
DIISOCYANATE AND VARIOUS AMINES

| Run No. | Amine | Wt % | | | Results |
|---------|--|-------|-----------------------------|--------------------|--|
| | | Amine | p-Phenylene Diisocyanate | Total Additives | |
| 5-7-1 | Diam 21 (N-Coco-1, 3-propylene Diamine) | 2.46 | 1.46 | 3.92 | Ppt. formed immediately. |
| 5-7-2 | Diam 11 (N-Oleyl-1, 3-propylene Diamine) | 2.78 | 1.24 | 4.02 | Formed a weak gel. Breaks on standing. |
| 5-7-3 | Diam 26 (N-Tallow-1, 3-propylene Diamine) | 2.74 | 1.25 | 3.99 | Formed a weak gel. Somewhat better than Diam 11. |
| 5-7-4 | Alamine 4D (Lauryl primary amine) | 2.8 | 1.2 | 4.0 | Formed a swollen, solid slurry. |
| 5-7-5 | Alamine 21D (Coco primary amine) | 2.84 | 1.15 | 3.99 | Formed a solid slurry. |
| 5-8-6 | Alamine 11D (Oleyl primary amine) | 3.08 | 0.92 | 4.0 | Formed a weak gel. Somewhat better than Diam 11. |
| 5-8-9 | Ethylene Diamine | 1.08 | 2.92 | 4.0 | Formed ppt. |
| 5-8-10 | Diethylene Triamine | 1.56 | 2.43 | 3.99 | Formed ppt. |

TABLE 13
GELATION OF JP-4 BY USING 2,6-TOLYLENE DIISOCYANATE AND VARIOUS AMINES

| Run No. | Wt % Diisocyanate | Amine | Wt % | | Results |
|---------|-------------------|-------------------------------|-------|-----------------|---|
| | | | Amine | Total Additives | |
| 5-24-1 | 1.3 | Lauryl Amine (Alamine-4D) | 2.7 | 4.0 | Instantly gels the fuel. Reaction too rapid to obtain good mixing. |
| 5-24-2 | 0.65 | " | 1.35 | 2.0 | Same as above. |
| 5-24-3 | 1.65* | " | 1.35 | 2.0 | A firm gel was obtained. |
| 5-24-4 | 1.0 | Oleyl Amine | 3.0 | 4.0 | Gave a clear, weak gel. The gel was somewhat elastic. |
| 5-24-6 | 1.0 | Dimer Diamine | 3.0 | 4.0 | Instantly gelled the fuel. Reaction too rapid to obtain good mixing. |
| 5-24-7 | 1.3 | N-Coco-1,3-propylene diamine | 2.7 | 4.0 | Produced a voluminous ppt. |
| 5-24-8 | 1.1 | N-Oleyl-1,3-propylene diamine | 2.9 | 4.0 | Flocculent ppt. |

*10% n-propyl thiolchloroformate (based on diisocyanate) was added in order to retard the reaction.

TABLE 14
GELATION OF JP-4 BY USING VARIOUS ISOMERS OF TOLYLENE
DIISOCYANATE AND LAURYL AMINE

| Run No. | Tolylene Diisocyanate | | Alamine 4D (Lauryl Amine) Wt % | Wt % Total Additives | Results |
|------------|-----------------------|--------------------|--------------------------------------|----------------------------|---|
| | Wt % 2,4-Isomer | Wt % 2,6-Isomer | | | |
| 5-26-1 | 1.3 | - | 2.7 | 4.0 | Product soluble in JP-4 |
| 5-26-2 | 1.04 | 0.26 | 2.7 | 4.0 | A weak gel forms rather slowly (> 1 min.). |
| 5-26-3 | 0.85 | 0.45 | 2.7 | 4.0 | A firm gel is formed in 1 to 2 seconds. |
| 5-24-1 | - | 1.3 | 2.7 | 4.0 | Instantly gels. Reacts too fast to obtain good mixing. |
| 5-24-3 | - | 0.65* | 1.35 | 2.0 | A firm gel is formed in about 1 second. |

*10% n-propyl thiolchloroformate (based on diisocyanate) was added in order to retard the reaction.

TABLE 15
ATTEMPTED GELATION OF JP-4 BY USING DIMER DIAMINE AND VARIOUS ISOCYANATES

| Run No. | Wt % Dimer Diamine* | Isocyanate | Wt % | | Results |
|---------|---------------------|-----------------------------|------------|-----------------|-------------------------------------|
| | | | Isocyanate | Total Additives | |
| 5-16-1 | 3.09 | Hylene TM-65** | 0.91 | 4.0 | Forms ppt. |
| 5-16-2 | 2.51 | " | 1.49 | 4.0 | " |
| 5-16-4 | 3.11 | Hexamethylene Diisocyanate | 0.89 | 4.0 | Forms a highly swollen ppt. |
| 5-16-5 | 2.55 | " | 1.45 | 4.0 | " |
| 5-17-7 | 3.13 | m-Phenylene Diisocyanate | 0.87 | 4.0 | " |
| 5-17-9 | 2.51 | 2,4-Tolylene Diisocyanate | 1.49 | 4.0 | Forms a ppt. |
| 5-17-10 | 2.21 | Phenyl Isocyanate | 1.79 | 4.0 | Formed an oily, immiscible product. |
| 5-17-11 | 2.78 | 1,3,5-Benzene Triisocyanate | 1.22 | 4.0 | Formed a slightly swollen ppt. |

*Diamine made from Dimer Acids (Emery Industries).

**65% 2,4-Tolylene Diisocyanate; 35% 2,6-Tolylene Diisocyanate (Du Pont).

TABLE 16
ATTEMPTED FUEL GELATION BY USING m-XYLENE DIAMINE
AND VARIOUS DIISOCYANATES

| Run No. | Diisocyanate | Wt % Diisocyanate | Wt % m-Xylene Diamine | Wt % Total Additives | Results |
|---------|----------------------------|-------------------|-----------------------|----------------------|-------------|
| 5-9-A1 | Hylene TM-65* | 2.25 | 1.75 | 4.0 | Formed ppt. |
| 5-9-A2 | " | 1.67 | 2.33 | 4.0 | " |
| 5-9-A3 | " | 2.88 | 1.12 | 4.0 | " |
| 5-9-B1 | Hylene T** | 2.25 | 1.75 | 4.0 | " |
| 5-9-B2 | " | 1.67 | 2.33 | 4.0 | " |
| 5-10-C1 | Hexamethylene Diisocyanate | 2.21 | 1.79 | 4.0 | " |
| 5-10-C2 | " | 1.53 | 2.47 | 4.0 | " |
| 5-10-C3 | " | 2.85 | 1.15 | 4.0 | " |

*Tolylene Diisocyanate: 65% 2,4-isomer; 35% 2,6-isomer.

**2,4-Tolylene Diisocyanate.

TABLE 17
URETHANE ELASTOMER (ADIPRENE L-100) FOR GELLING FUEL

| Run No. | Wt % Adiprene L-100* | Name of Compound 2 | Wt % | | Wt % Total Additives | Results |
|---------|----------------------|---------------------|------------|------------|----------------------|---------------------------------|
| | | | Compound 2 | Compound 2 | | |
| I-44-2 | 1.0 | Armeen 12 | 1.0 | | 2.0 | Solution clouded, no gel. |
| I-44-3 | 1.0 | Araldite DP-125** | 1.0 | | 2.0 | Gummy ppt. separated from fuel. |
| I-44-4 | 1.0 | Diethylene Triamine | 1.0 | | 2.0 | " " " " |
| I-44-5 | 1.0 | Genamid 250*** | 1.0 | | 2.0 | " " " " |

*Urethane elastomers (Du Pont).

**Polyamine Hardener (Ciba).

***Resinous Amine (General Mills).

TABLE 18
JP-4 GELATION BY USING NIAx-PPG-1025, HYLENE TM-65
PREPOLYMER WITH VARIOUS AMINES

| Run No. | Wt % Niax-1025- TM-65 Adduct | Name | Compound | Wt % Additives | Wt % Total Additives | Results |
|---------|---------------------------------|-------------|--|----------------|----------------------|------------------|
| 2-38-1 | 1.35 | Alamine 4D | Lauryl Amine | 0.36 | 1.71 | Weak gel. |
| 2-40-1 | 1.74 | Diam-21 | N-Coco-1,3-propylene diamine | 0.42 | 2.16 | Flocculent ppt. |
| 2-40-2 | 2.32 | Diam-11 | N-Oleyl-1,3-propylene diamine | .728 | 3.05 | Flocculent ppt. |
| 2-40-3 | 2.32 | Diam-26 | N-Tallow-1,3-propylene diamine | .71 | 3.03 | Flocculent ppt. |
| 2-40-5 | 2.32 | Alamine 21D | Coco primary amine | .80 | 3.12 | Weak gel. |
| 2-40-6 | 2.32 | Alamine 11D | Oleyl primary amine | 1.08 | 3.40 | Soluble in JP-4. |
| 2-40-7 | 2.32 | - | Methane Diamine | .04 | 2.36 | Ppt. |
| 2-41-8 | 2.32 | Armeen 18 | Mixture (C ₁₄ -C ₁₈) amines | 1.08 | 3.40 | Weak gel. |
| 2-41-9 | 2.32 | Armeen T | Mixture (C ₁₄ -C ₁₈) amines | 1.04 | 3.36 | Soluble in JP-4. |

TABLE 19
ATTEMPTED GELATION OF JP-4 BY USING NIAx-PPG-2025, HYLENE TM-65
ADDUCT WITH VARIOUS AMINES

| Run No. | Wt % Niax-2025 TM-65 Adduct | Compound B | Wt % | | Results |
|------------|-----------------------------------|--|------|--------------------|--------------------|
| | | | | Total Additives | |
| 2-15-1 | 2.0 | Menthane Diamine | 0.5 | 2.5 | Flocculent ppt. |
| 2-15-2 | 2.0 | Diethylene Tri- amine | 0.2 | 2.2 | Gummy ppt. |
| 2-15-3 | 2.0 | Armeen 12 | 1.0 | 3.0 | Thick slurry. |
| 2-16-5 | 2.0 | Duomeen S Amide of Empol 1014 | 0.5 | 2.5 | Reaction too slow. |
| 2-16-6 | 2.0 | Menthane Diamine Amide of Empol 1014 | 0.5 | 2.5 | Ppt. |

TABLE 20
ATTEMPTED GELATION OF JP-4 BY USING
VARIOUS POLYOL-HYLENE TM-65 ADDUCTS

| Run No. | Wt % Prepolymer | Coreactant | Wt % Coreactant | Wt % Catalyst* | Wt % Total Additives | Results |
|---------|--------------------|----------------------|--------------------|-------------------|----------------------------|---|
| 3-37-5 | 4.0** | Oleic Acid | 2.0 | 0.1 | 6.1 | Product apparently soluble. |
| 3-38-6 | 4.0** | Lauryl Amine | 2.0 | - | 6.0 | Voluminous ppt. |
| 3-38-7 | 4.0** | Diam 21 (diamine) | 2.0 | 0.1 | 6.1 | Rapidly formed a viscous insoluble polymer. |

*50:50 mixture of cobalt naphthenate and N-methylmorpholine.

**Prepolymer consisted of 0.2 mole Niax 1025 (a polyol); 0.02 mole glycerol; 0.46 mole Hylene TM-65.

TABLE 21
REACTION OF VARIOUS HYDROXYL COMPOUNDS WITH HYLENE TM-65 IN JP-4

| Run No. | Hydroxyl Compound Name | Wt % Hydroxyl Compound | Wt % Hylene TM-65 | Wt % Other Reactant | Wt % Catalyst* | Wt % Total Additives | Results |
|---------|------------------------|------------------------|-------------------|---------------------|----------------|----------------------|------------------|
| 4-6-1 | Pluracol TP 4040** | 4.0 | 2.0 | - | .1 | 6.1 | Product soluble. |
| 4-6-2 | Pluracol TPE 4542*** | 4.0 | 2.0 | - | .1 | 6.1 | " |
| 4-6-3 | Pluracol TP 1540† | 4.0 | 2.0 | - | .1 | 6.1 | " |
| 4-6-4 | Pluracol GP 3030‡ | 4.0 | 2.0 | - | .1 | 6.1 | " |

*4 parts cobalt naphthenate; 2 parts stannous octoate; 2 parts N-methylmorpholine.

**4000 mw polyoxypropylene derivative of trimethylolpropane.

***4500 mw polyoxypropylene derivative of trimethylolpropane terminated with ethylene oxide.

†1535 mw polyoxypropylene derivative of trimethylolpropane.

‡3000 mw polyoxypropylene derivative of glycerol.

TABLE 22
ETHOMEENS AS POTENTIAL GELLING AGENTS FOR JP-4

| Run No. | Ethomeen | Wt % Ethomeen | Wt % Hylene TM-65 | Wt % Catalyst* | Wt % Total Additives | Results |
|---------|----------------|---------------|-------------------|----------------|----------------------|--|
| 4-7-1 | Ethomeen C/20 | 3.25 | .87 | 0.25 | 4.37 | Immediate clouding of JP-4. Polymer ppt'd. as an oil in 1 - 2 minutes. |
| 4-7-2 | Ethomeen C/12 | 2.85 | 1.74 | 0.25 | 4.84 | Product soluble. |
| 4-7-3 | Ethomeen T/15 | 3.61 | 1.29 | 0.25 | 5.15 | Product soluble. |
| 4-7-4 | Ethomeen T/20 | 4.3 | 1.29 | 0.25 | 5.84 | Polymer ppt'd. as a viscous semi-solid. |
| 4-8-5 | Ethomeen S/12 | 3.5 | 1.74 | 0.25 | 5.49 | Product soluble. |
| 4-8-6 | Ethomeen S/20 | 3.55 | 0.87 | 0.25 | 4.67 | Polymer ppt'd. as a viscous semi-solid. |
| 4-9-9 | Ethomeen S/15 | 3.15 | 1.29 | 0.25 | 4.69 | Polymer ppt'd. as a viscous semi-solid. |
| 4-9-10 | Ethomeen 18/12 | 2.70 | 1.29 | 0.25 | 4.24 | Product soluble. |

*Catalyst consists of 2 parts N-methylmorpholine; 4 parts cobalt naphthenate; 2 parts stannous octoate.

TABLE 23
ATTEMPTS TO GEL JP-4 BY USING VARIOUS PROPOMEENS
AND TOLYLENE DIISOCYANATE

| Run No. | Propomeen | Wt% | Wt % Hylene TM-65 | Wt % Catalyst | Wt % Total Additives | Results |
|---------|-----------|-----|-------------------|---------------|----------------------|--------------------------|
| 3-4-6 | C/12* | 2.5 | 1.5 | 0.4 | 4.4 | Product soluble in fuel. |
| 3-5-7 | C/25** | 3.4 | 0.61 | 0.4 | 4.41 | Flocculent ppt. |
| 3-5-8 | HT/12*** | 2.6 | 1.4 | 0.4 | 4.40 | Product soluble in fuel. |

*Coco amine with 2 moles combined propylene oxide.

**Coco amine with 15 moles combined propylene oxide.

***Hydrogenated Tallow amine with 2 moles combined propylene oxide.

†Volume ratio: 3 parts water; 2 parts N-methylmorpholine; 2 parts triethylamine; 1 part stannous octoate.

TABLE 24
GELATION OF JP-4 BY USING
PROPOMEEN HT/12-NACCONATE 80 ADDUCT WITH VARIOUS AMINES

| Run No. | Wt % Adduct | Amine | Wt % Amine | Wt % Total Additives | Results |
|---------|----------------|---|---------------|----------------------------|------------------|
| 2-52-1 | 1.6 | Diam-21 (N-oleyl-1, 3- propylene diamine) | .69 | 2.29 | Soluble. |
| 2-52-3 | 1.44 | Diam-26 (N-Tallow-1, 3- propylene diamine) | .80 | 2.24 | Soluble. |
| 2-52-4 | 1.28 | Alamine-4D (Lauryl amine) | .79 | 2.07 | Formed thin gel. |
| 2-52-7 | 1.61 | Menthane diamine | .78 | 2.39 | Formed fine ppt. |
| 2-52-9 | 1.79 | Armeen 18 (Octadecyl amine) | 1.08 | 2.87 | Formed thin gel. |
| 2-52-10 | 1.28 | Armeen T (Tallow amine) | 1.04 | 2.32 | Soluble. |
| 2-52-11 | 1.28 | Armeen HT (Hydrogenated Tallow amine) | 1.04 | 2.32 | Formed thin gel. |
| 2-52-14 | 1.28 | Armeen 12 (Dodecyl amine) | .74 | 2.02 | Formed thin gel. |

TABLE 25
GELATION OF JP-4 BY USING PROPOMEEN C/12-NACCONATE
80 ADDUCT WITH VARIOUS AMINES

| Run No. | Wt % Adduct | Amine | Wt % Amine | Wt % Total Additive | Results |
|---------|-------------|--|------------|---------------------|---------------------------------------|
| 2-51-1 | 1.67 | Diam-21 (N-Coco-1,3-propylene diamine) | .70 | 2.37 | Flocculent ppt. thickens on standing. |
| 2-51-3 | 1.50 | Diam-26 (N-Tallow-1,3-propylene diamine) | .80 | 2.30 | Flocculent ppt. |
| 2-51-4 | 1.33 | Alamine 4D(Lauryl amine) | .76 | 2.09 | Ppt. |
| 2-51-5 | 1.33 | Alamine 21D(Coco Amine) | .80 | 2.13 | Ppt. |
| 2-51-8 | 1.67 | Menthane diamine | .58 | 2.25 | Thick, heavy ppt. |
| 2-51-10 | 1.33 | Armeen 18 (Octadecyl amine) | 1.08 | 2.41 | Soluble. |
| 2-51-11 | 1.33 | Armeen T (Tallow amine) | 1.04 | 2.37 | Soluble. |
| 2-51-12 | 1.33 | Armeen HT (Hydrogenated Tallow amine) | 1.04 | 2.37 | Soluble. |
| 2-51-15 | 1.33 | Armeen 12 (Dodecyl amine) | .74 | 2.07 | Flocculent ppt. |

TABLE 26
GELATION OF JP-4 BY USING PROPOMEEN HT/12-POLYOL-
HYLENE TM-65 ADDUCTS WITH VARIOUS AMINES

| Run No. | Wt % Adduct | Amine | Wt % | Wt % | | Results |
|------------|----------------|-----------|------|-------|-----------|--|
| | | | | Total | Additives | |
| 3-24-1 | 2.5* | Lauryl | 1.5 | 4.0 | | Rapidly gelled fuel. Gel inferior to C ₁₈ amine-Tolylene Diisocyanate adduct. |
| 3-24-2 | 2.3* | Octadecyl | 1.7 | 4.0 | | Same as above. |
| 3-24-3 | 2.4** | Lauryl | 1.6 | 4.0 | | Same as above. |
| 3-24-4 | 2.15** | Octadecyl | 1.85 | 4.0 | | Somewhat slower in gelling fuel. Gel equivalent to C ₁₈ amine-Tolylene Diisocyanate adduct. |

*Prepolymer consisting of 0.33 mole Hylene TM-65; 0.1 mole Propomeen HT/12; 0.05 mole Niax
150 NCO eq/gm = 0.0032.
**Prepolymer consisting of 0.38 mole Hylene TM-65; 0.1 mole Propomeen HT/12; 0.017 mole Niax
168 NCO eq/gm = 0.0037.

TABLE 27
ATTEMPTED SOLIDIFICATION OF JP-4 BY USING VARIOUS ACIDS

| Run No. | Acid | Wt % | Coreactant | Wt % | Wt % Catalyst | Wt % Total Additives | Results |
|---------|-----------------|------|----------------------------|------|---------------|----------------------|---|
| 3-9-1 | Oleic | 1.0 | Niax 1025-TM-65 prepolymer | 2.0 | 0.5* | 3.5 | Slight clouding of JP-4. |
| 3-9-2 | Dimer Acid 1014 | 2.0 | " " | 2.0 | 0.5* | 4.5 | Soluble product. |
| 3-10-1 | Lauric | 2.0 | Hylene TM-65 | 1.0 | 0.5* | 3.5 | CO ₂ evolution with formation of precipitate. |
| 3-10-2 | Dimer Acid 1014 | 2.0 | Hylene TM-65 | 1.0 | 0.5* | 3.5 | CO ₂ evolution with formation of voluminous ppt. |
| 3-10-3 | Oleic | 3.0 | Hylene TM-65 | 1.0 | 0.5* | 4.5 | Same as 3-10-2. |

*70:30 mixture of cobalt naphthenate and N-methylmorpholine.

TABLE 28
VARIOUS METHACRYLATE AND ACRYLATE COPOLYMERS
AS POTENTIAL GELLING AGENTS

| Run No. | Reactant A | Wt % | | Wt % | | Results |
|---------|--|------------|---------------------|------------|-----------------|--|
| | | Reactant A | Tetrabutyl Titanate | Reactant A | Total Additives | |
| 4-1-1 | Hydrolyzed poly (Isobutyl methacrylate) Acid No. = 0.65 | 4.0 | 0.9 | 4.9 | 4.9 | Converted JP-4 to a viscous fluid. |
| 4-1-2 | Hydrolyzed poly (Isobutyl methacrylate) Acid No. = 0.52 | 4.0 | 0.71 | 4.71 | 4.71 | Converted JP-4 to a lumpy, viscous fluid. |
| 4-1-3 | Acrylic Acid-2-ethylhexyl acrylate copolymer* Acid No. = 0.50 | 4.0 | .68 | 4.68 | 4.68 | Converted JP-4 to a viscous fluid. Agitation yielded a tough, elastic gel. |
| 4-2-5 | " " " " | 6.0 | 1.0 | 7.0 | 7.0 | Tough rubbery gel with stirring. |
| 4-2-6 | " " " " | 10.0 | 1.7 | 11.7 | 11.7 | Converted fuel to a dry, crumbly mass with stirring. |

*Solution polymerization of .05 mole acrylic acid and 0.50 mole 2-ethylhexyl acrylate.

TABLE 29
GELATION OF JP-4 BY USING n-PROPYL THIOLCHLOROFORMATE
AND VARIOUS AMINES

| Run No. | Wt % Thiolschloroformate | Amine | Wt % | | Results |
|---------|--------------------------|---|-------|-----------------|--|
| | | | Amine | Total Additives | |
| 5-25-1 | 1.4 | N-Coco-1,3-propylene diamine (Diam-21) | 2.7 | 4.1 | Slight increase in fuel viscosity. No gel. |
| 5-25-2 | 1.4 | N-Oleyl-1,3-propylene diamine (Diam-11) | 3.6 | 5.0 | " " " |
| 5-25-3 | 1.4 | Coco-amine (Alamine-21D) | 2.0 | 3.4 | Formed a weak gel. |
| 5-25-4 | 1.4 | Lauryl amine (Alamine-4D) | 2.0 | 3.4 | Formed a slight ppt. No gel. |
| 5-25-5 | 1.4 | Dimer amine | 2.9 | 4.3 | Formed a voluminous ppt. No gel. |
| 5-25-6 | 1.4 | Oleyl amine (Alamine-11D) | 2.7 | 4.1 | Product soluble. |
| 5-25-7 | 2.3 | Ethylene diamine | 1.0 | 3.3 | " " |

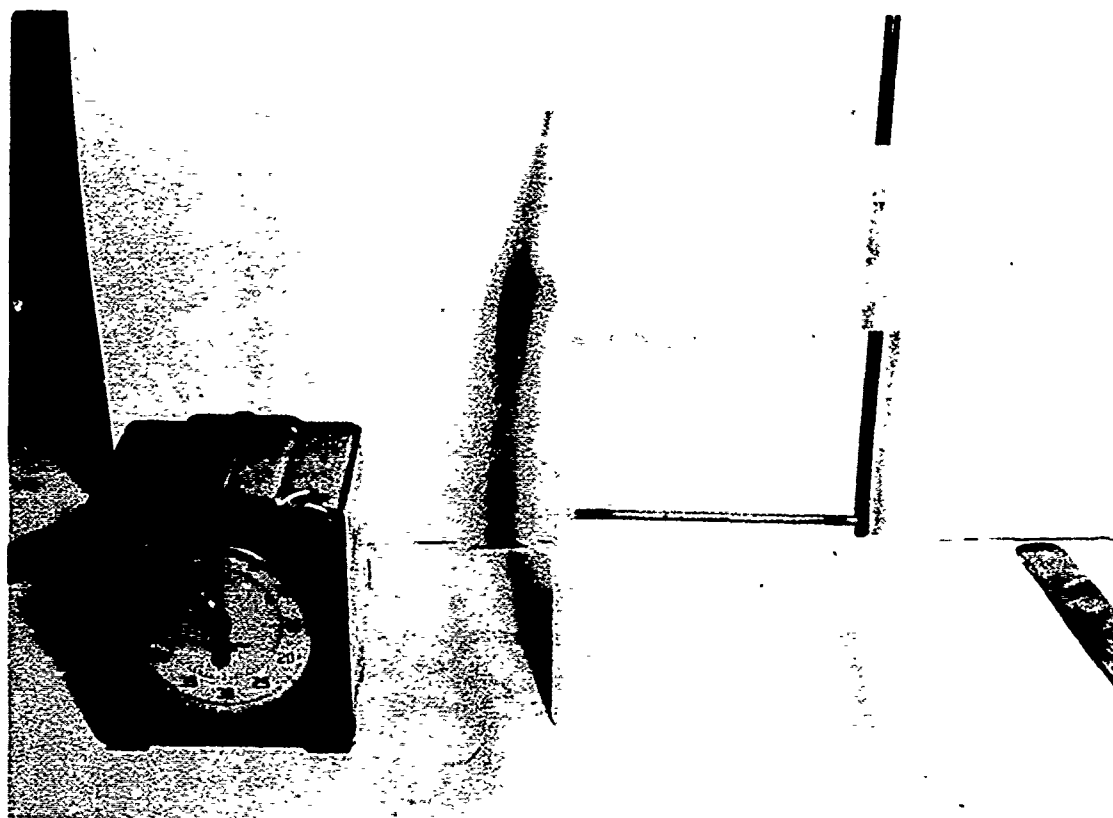


FIGURE 1. BENCH SCALE EQUIPMENT FOR
TESTING FUEL SOLIDIFICATION



FIGURE 2. FUEL GEL

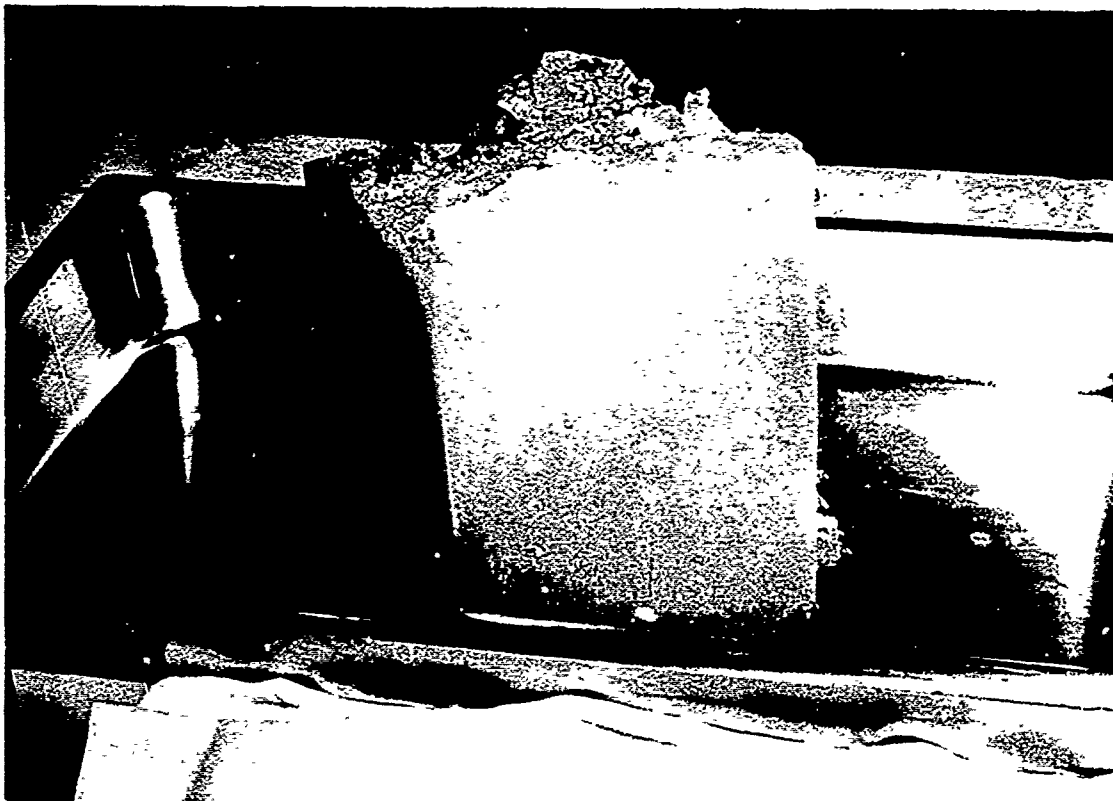


FIGURE 3. UNSUPPORTED GELLED FUEL



FIGURE 4. SOLIDIFIED FUEL

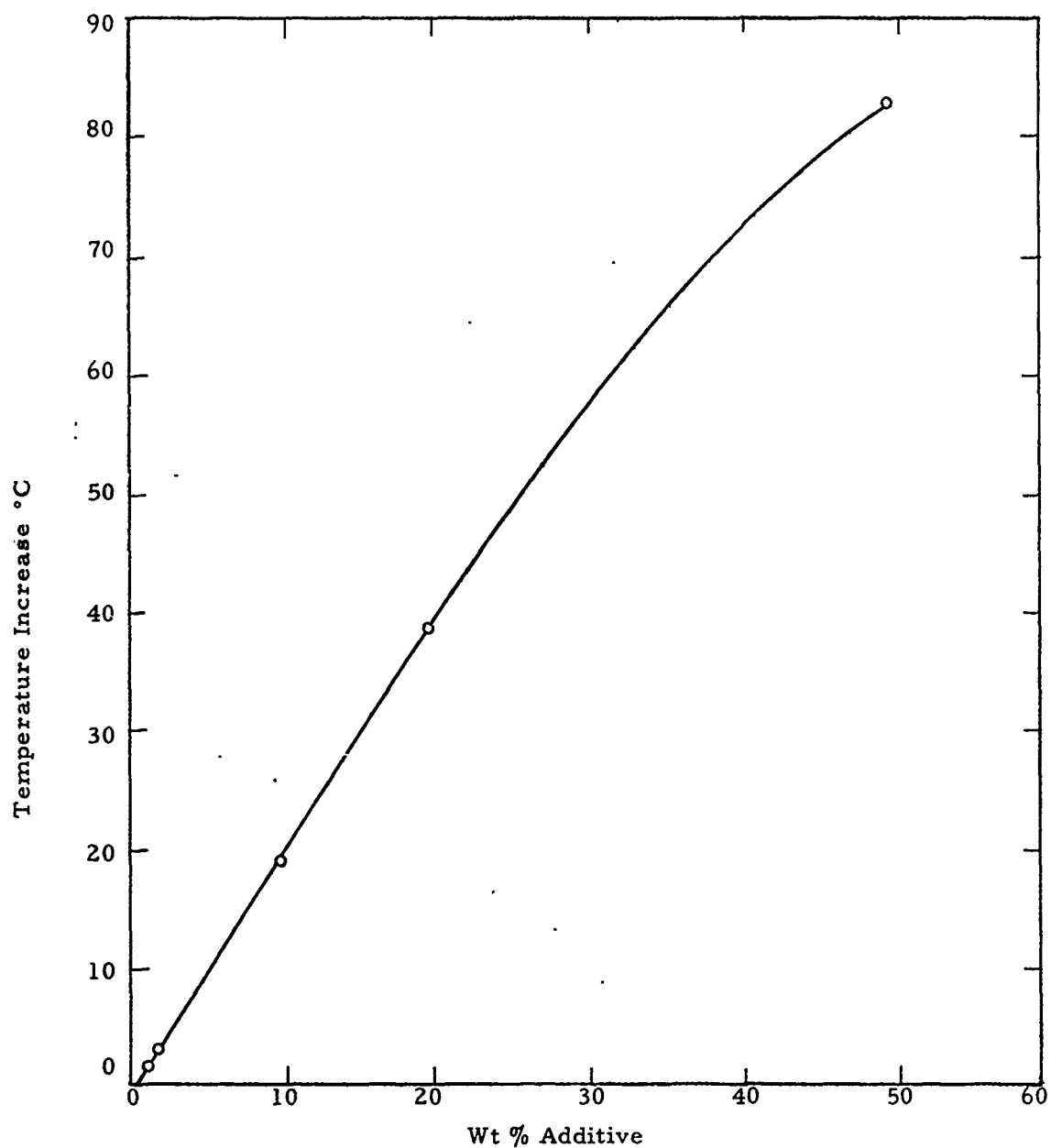


FIGURE 5. HEAT OF REACTION FOR LAURYL AMINE-TOLYLENE DIISOCYANATE IN JP-4

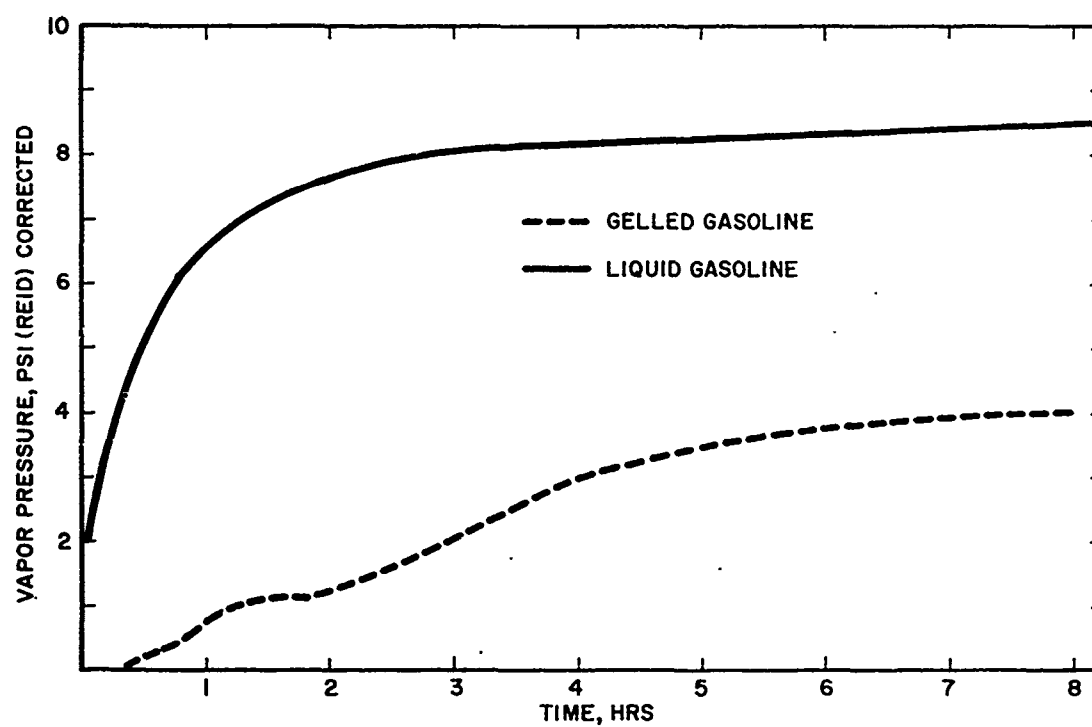


FIGURE 6. VAPOR PRESSURE OF GASOLINE
AND GELLED GASOLINE

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Unclassified Report

Progress is reported on rapid methods for gelling aircraft fuels. One of the more promising systems developed is the use of fatty amines and tolylene diisocyanates. Systems were developed that will gel fuel with as low as 1.0 weight percent additives. The rate of gelation and the (over)

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This gelation process significantly decreases the vapor pressure of the fuel and thus greatly reduces the fire hazard caused by fuel misting.

Other fuel gelling systems have been developed. At a 4 percent concentration, the reaction product of an acrylic acid copolymer and n-tetrabutyl titanate in JP-4 produces an elastic gel having excellent strength.

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